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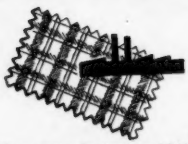

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VOL. XIX, NO. 9 September, 1949

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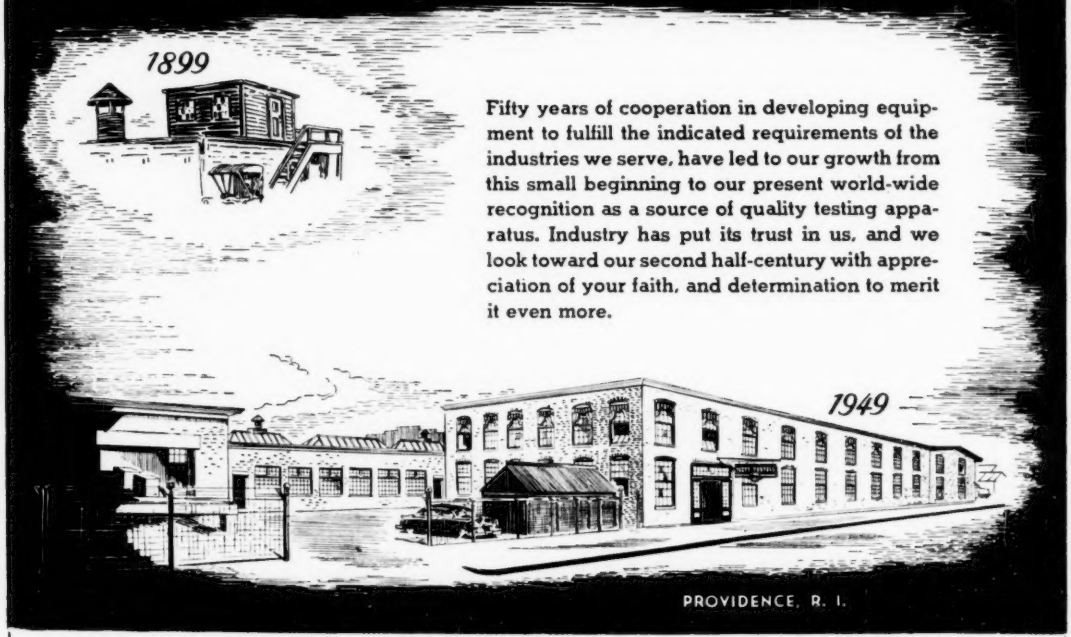

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TEXTILE RESEARCH JOURNAL

VOL. XIX, NO. 9 SEPTEMBER, 1949

The Autoxidation of Alkali Cellulose

Part I: An Experimental Study of the Kinetics of the Reaction*

D. Entwistle, E. H. Cole, and N. S. Wooding

Courtaulds, Limited, Coventry, England

Abstract

The kinetics of the uncatalyzed oxidation of alkali cellulose by molecular oxygen (autoxidation) have been studied. It is shown that a linear relationship exists between the copper number of cellulose regenerated from a freshly prepared alkali cellulose and the initial rate of autoxidation of the alkali cellulose. As reaction proceeds, however, the rate approaches a constant value which, under given conditions, is independent of the initial copper number. Peroxides are formed during the reaction, to an extent which is dependent upon trace concentrations of various heavy metals. The effects of temperature, oxygen pressure, and alkali cellulose composition on reaction rate are discussed. The results are consistent with the present picture of autoxidation processes being free-radical-propagated chain reactions.

Introduction

In recent years considerable advances have been made in the theory of oxidation processes—based on more precise knowledge of the nature of free-radical reactions on the one hand, and of electron transfer processes on the other. It has become abundantly clear that direct oxidations with molecular oxygen are chain reactions which involve free radicals [26].

The autoxidation of olefinic hydrocarbons has received particular attention [1, 11, 19] and is thought to occur by the following sequence of processes:

$$R{-}H + O_2 \xrightarrow{\text{(slow)}} R{-} + HO_2, \qquad (1)$$

where H is the relatively labile hydrogen in the α-position to the double bond. It is important to recognize that this, the initial reaction of autoxidation, occurs between an organic molecule and a diatomic oxygen molecule. It must be feasible both in terms of energy and of reaction mechanism considerations, and it seems unlikely, therefore, that this primary process results in the direct formation

* Part II will appear in the October, 1949, issue of TEXTILE RESEARCH JOURNAL.

of a hydroperoxide, as has sometimes been suggested. The sequence of reactions then continues:

$$R\cdot + O_2 \xrightarrow{\text{(fast)}} R{-}O{-}O\cdot \qquad (2)$$

$$R{-}O{-}O\cdot + RH \xrightarrow{\text{(fast)}} ROOH + R\cdot \qquad (3)$$

and oxygen continues to be absorbed by alternation of processes (2) and (3) until the sequence is broken by radical association or some other chain-terminating process. Such reactions are normally autocatalytic. The O—O bond of the hydroperoxide ROOH has much less than half the strength of the double bond of the oxygen molecule; its dissociation energy has been variously estimated at between 35 and 56 kg. cals., and the activation energies of the thermal decomposition of many hydroperoxides lie between 17 and 25 kg. cals. It is considered, therefore, that the autocatalysis is due to occasional thermal fission of this bond:

$$R{-}O{-}OH \rightarrow R{-}O\cdot + \cdot OH,$$

with consequent slow chain branching [11, 19].

Hydroperoxide decomposition is catalyzed by ions of the transition metals [12, 19] by some process such as:

$$ROOH + M^{++} \rightarrow RO\cdot + M^{+++} + \cdot OH.$$

Waters [19] suggested this as an explanation for the observation that the catalysis of tetralin autoxidation by the transition metals is most apparent in the secondary stage of the reaction, when appreciable hydroperoxide formation has occurred.

This general picture of autoxidation as a free-radical-propagated chain process now rests on a broad basis of experimental evidence, much of which will be quoted in the Discussion section of this paper.

Oxidation of cellulose by atmospheric oxygen occurs under a variety of conditions. Pure neutral cellulose is stable in air at room temperature. In the temperature range 100–120°C. autoxidation occurs with appreciable velocity and is accelerated by the presence of moisture [7, 23]. Cellulose undergoes a photosensitized autoxidation at room temperature, particularly in the presence of certain vat dyestuffs [24]; here also, moisture may play an important part. Autoxidation of the leuco compounds of some vat dyestuffs [2] and of drying oils may induce the autoxidation of a cellulose substrate [22]. The autoxidation of cellulose under alkaline conditions, in cuprammonium hydroxide solution or as alkali cellulose, has an extensive treatment in the literature. The latter reaction has long been accepted by the viscose industry as the most convenient method of obtaining progressive, controlled depolymerization of cellulose. Despite its great technological importance, however, no completely satisfactory account of either the oxidation process or the resultant depolymerization has yet been given.

The autoxidation of alkali cellulose will be discussed here in the light of existing published work and also of new evidence, which is presented. All the evidence is consistent with the hypothesis that the reaction is a chain process involving free radicals. The reaction has been studied by a simple manometric technique, and it is hoped that the results obtained may be useful in building up a more general picture of the mechanism of cellulose autoxidation.

A Relationship Between the Reducing Power of Cellulose and the Autoxidation Characteristics of the Derived Alkali Cellulose

It became evident early in this work that the rate of oxygen absorption by alkali cellulose, as well as being a function of temperature and oxygen pressure, was also a function of time during the early stages of the reaction. In order to obtain a clear picture of this effect, alkali celluloses of a composition standard in the viscose rayon industry (*viz.*, 30% cellulose, 15% sodium hydroxide, and 55% water) were prepared from a series of commercially available rayon pulps, and the variation with time of their rates of autoxidation was studied at a constant oxygen pressure of 700 mm. of mercury, at 25°C and 35°C. Measurements were carried out using the absorptiometer illustrated in Figure 1 and described in detail in the Experimental Procedure section of this paper. Results for all these pulps are given in Table I and a selected few are shown graphically in Figures 2 and 3. The initial autoxidation rate varies between wide limits for the different cellulose samples, but all the rates converge as the reaction proceeds and ultimately lie in a narrow range of velocities which then remain approximately constant up to oxygen consumption as high as 50

ml. of oxygen (n.t.p.) per g. of cellulose (see also Davidson [5].

Qualitatively, these results indicate that alkali celluloses from bleached cotton pulps have the lowest rates of autoxidation, while the highest rates are shown by alkali celluloses from the less refined wood pulps. Quantitatively, a linear relation is found between the copper numbers of the celluloses regenerated from the freshly prepared alkali celluloses and the initial rates of alkali cellulose autoxidation (Figure 4). (The copper number of a sample of cellulose is defined as the number of g. of copper reduced from the cupric to the cuprous state in alkaline solution under standard conditions by 100 g. of the cellulose.) In order to study this relationship further a standard cellulose of very low copper number was prepared by boiling a quantity of Egyptian cotton (Giza 7) with 2% caustic soda for 4 hours at an excess pressure of 30 lb. per square inch, followed by prolonged washing to neutrality. From this material, ranges of samples of modified celluloses of increasing copper number were prepared by graded acid hydrolysis and by graded bleaching and other oxidizing treatments. Alkali celluloses of the standard composition were prepared from them and the variation of their autoxidation rates with time was studied at 25°C and an oxygen pressure of 700 mm. of mercury. The copper numbers of celluloses regenerated from these alkali celluloses immediately after preparation were also determined. Results are given in Table II and in Figures 5 and 6. The relationship between initial autoxidation rate and copper number for many of these experimental alkali celluloses is closely similar to that obtained for the commercial cellulose pulps. The only notable exceptions are the alkali celluloses prepared from periodate modified cellulose. The autoxidation rates of alkali celluloses derived from the various bleached and acid-hydrolyzed cottons rapidly converged to a common steady value similar to that shown by the commercial pulps. It is interesting to note (Figure 7) that the alkali celluloses prepared from the unmodified cotton of copper number 0.05 showed a well-defined induction period of up to 100 minutes during which no appreciable reaction occurred in their autoxidation at 25°C. Such a phenomenon is characteristic of many autoxidations known to proceed by a free-radical chain mechanism. An induction period may be indicative either of the presence of an inhibitor, which is destroyed as reaction proceeds, or of a truly autocatalytic process. In the present case the progressive reduction in initial reaction rate with decreasing reducing value suggests that an autocatalytic process is concerned. It has been maintained by many workers that the hot alkaline treatment of a modified cellulose, which is involved in the copper-number determination, renders the result of doubtful value for calculation of the aldehyde-group content of the material. It is generally agreed that the hot alkaline copper reagent not only gives stoichiometric oxidation of aldehyde to carboxyl groups in a reducing cellulose, but also oxidizes those other structures which are produced by progressive alkaline modification. Aldehyde-group content of cellulose, calculated from copper number on the assumption of stoichiometric oxidation of aldehyde to carboxyl only, will therefore generally give too high a value. The extent of this discrepancy is in doubt, as there has not yet been an unequivocal determination of aldehyde-group content of cellulose. Other experiments, not described here, showed that for the present type of modified cellulose the reducing value determined by the copper-number technique exceeded that from milder oxidation by cold dilute

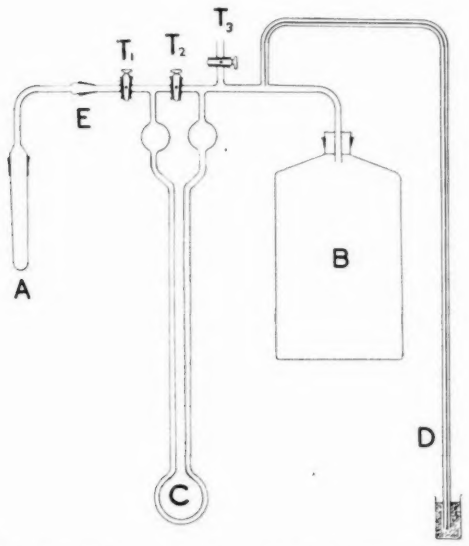


FIG. 1. *Apparatus used to study the absorption of oxygen at constant pressure by alkali cellulose.*

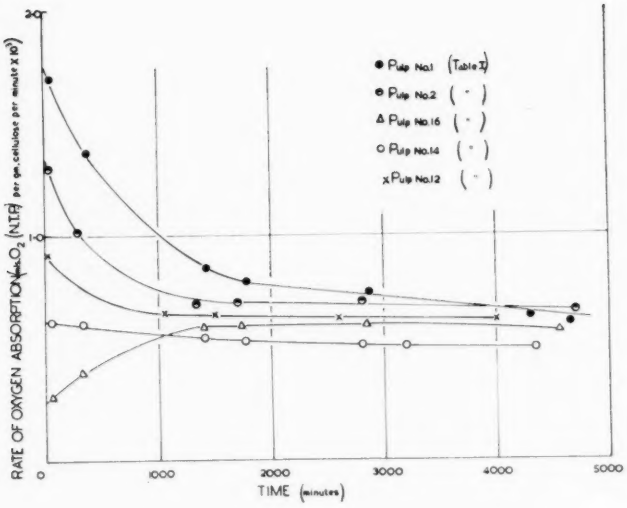


FIG. 2. *Variation with time of rates of autoxidation of alkali celluloses made from various pulps (at 25°C and constant* $P_{O_2} = 700$ *mm. Hg).*

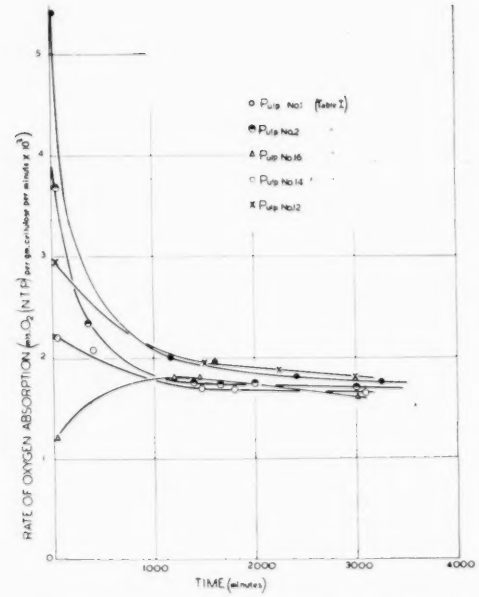


FIG. 3. *Variation with time of rates of autoxidation of alkali celluloses made from various pulps (at 35°C and constant* $P_{O_2} = 700$ *mm. Hg).*

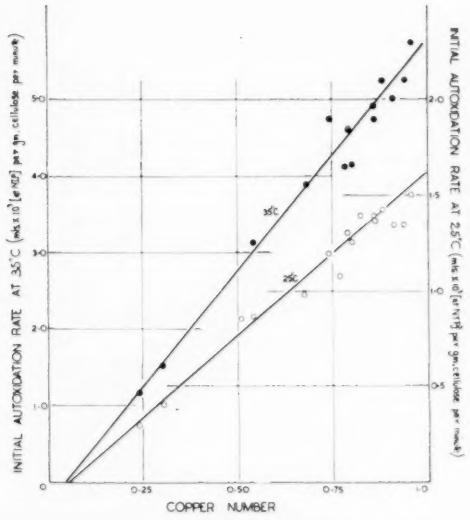


FIG. 4. *Relation between initial autoxidation rate of alkali cellulose and copper number of cellulose regenerated from it, for various commercial pulps (at 25°C and constant* $P_{O_2} = 700$ *mm. Hg).*

TABLE I

Pulp No.	Description of pulp	α-cell. on bone-dry pulp (%)	Copper No. On pulp	Copper No. On cell. regenerated from freshly prepared alk. cell.	$10^3 \times$ velocity coefficient of oxygen absorption by alk. cell. (ml. (n.t.p.) per min. per g. cell.) 25°C Initial	25°C At 4,000 min.	35°C Initial	35°C At 2,000 min.	Initial d(fluidity)/dt
1	Canadian Western hemlock, bleached sulfite pulp	92.0	2.38	0.96	1.71	0.60	5.7	1.70	0.021
2	Canadian spruce, bleached sulfite pulp	91.8	1.84	0.80	1.35	0.64	3.68	1.71	0.011
3	Canadian spruce, bleached sulfite pulp	92.0	1.65	0.79	1.31	0.62	4.62	1.80	0.013
4	Scandinavian spruce, bleached sulfite pulp	91.0	2.15	0.88	1.43	0.61	5.22	1.80	0.015
5	Scandinavian spruce, bleached sulfite pulp	91.5	2.22	0.91	1.36	0.62	4.95	1.64	0.013
6	Scandinavian spruce, bleached sulfite pulp	92.0	1.83	0.86	1.23	0.50	4.90	1.63	0.011
7	Scandinavian spruce, bleached sulfite pulp	90.8	2.13	0.86	1.39	0.60	4.70	1.80	0.007
8	Scandinavian spruce, bleached sulfite pulp	91.8	2.20	0.94	1.35	0.54	5.27	1.63	0 011
9	Scandinavian spruce, bleached sulfite pulp	91.0	2.08	0.82	1.33	0.64	3.75	1.81	0.010
10	Scandinavian spruce, bleached sulfite pulp	91.6	1.80	0.74	1.35	0.60	4.9	2.00	0.0099
11	Scandinavian spruce, "hot alkali purified" and bleached sulfite pulps	—	1.49	0.77	1.08	0.62	4.13	1.81	0.0089
12	Canadian spruce, "alkali purified" and bleached sulfite pulp	95.1	1.39	0.68	0.98	0.57	3.0	1.70	0.010
13	Scandinavian spruce, alkali purified and bleached sulfite pulp	94.5	0.96	0.54	0.87	0.62	3.16	1.80	0.0075
14	Scandinavian pine, sulfate pulp	95.0	0.86	0.51	0.62	0.49	2.28	1.70	0.0078
15	Kiered and bleached cotton	98.0	0.54	0.30	0.38	0.50	1.55	—	0.0055
16	Kiered and bleached cotton linters	98.1	0.28	0.24	0.30	0.56	1.15	1.80	0.0066
17	Pulp No. 2, kiered in laboratory	—	—	0.42	—	—	—	—	0.0053

permanganate [10] or hypoiodite [15] by now more than 15%. This element of doubt is not, however, relevant to the argument given below.

The aldehyde-group content corresponding to unit copper number would require 0.9 ml. of oxygen at n.t.p. per g. cellulose to oxidize it to carboxyl, a process which would require approximately 600 minutes for such an alkali cellulose under the present experimental conditions. It is important to show that such a reaction is not, in fact, a major cause of oxygen absorption, but that this produces more drastic changes in the cellulose structure from the beginning of the reaction. Figure 8 indicates the way in which aldehyde-group content, carboxyl-group content, intrinsic viscosity of the cellulose in cuprammonium, and oxygen absorption vary with time in the autoxidation of alkali cellulose. Only a small fraction of the absorbed oxygen is consumed in carboxyl-group production—much more is consumed in aldehyde-group production—and there is an oxygen consumption of almost 60% of the total unaccounted for by such processes. This oxygen surplus is even greater when it is remembered that copper number gives a higher value for aldehyde-group content. The production of carboxyl from aldehyde groups accounts for only approximately 10% of the total oxygen consumption.

Figure 9 shows that there is a good correlation between the initial rates of autoxidation and of the fluidity rise for the commercial pulps listed in Table I. This relation was confirmed in a satisfactory manner by comparing the rates of autoxidation and of fluidity rise for alkali celluloses prepared from a kiered cotton of very low copper number and from the same cotton after a hypochlorite bleaching treatment (samples 1 and 2 of Figure 5). These two alkali celluloses autoxidized at quite different rates (Figure 10*a* and *b*) and their fluidity-time relationships were also distinct (Figure 10*c*). The relationships between the fluidity increase and the amount of oxygen absorbed were, however, identical (Figure 10*d*). It seems likely, therefore, that the initial process in the autoxidation of alkali cellulose is a reaction of molecular oxygen with an aldehydic reducing group, and that this process initiates some chain reaction which results in far-reaching modification and breakdown of the cellulose molecule.

Present knowledge of autoxidation reactions in general and the shapes of the initial portions of the autoxidation rate curves of various alkali celluloses

TABLE II. RELATION BETWEEN CELLULOSE MODIFICATION AND INITIAL AUTOXIDATION RATE OF ALKALI CELLULOSE

	Sample	Initial autoxidation rate of derived alk. cell. at 25°C and P_{O_2} = 700 mm. Hg (ml. O_2 n.t.p./ min./g. cell.)	Copper No. of cell. from freshly prepared alk. cell.
1	Cotton (Giza 7), purified by alkaline kier boil	0	0.06
2	Cotton, hydrolyzed by *N* HCl	0.49×10^{-3}	0.28
3	Cotton, hydrolyzed by *N* HCl	0.80×10^{-3}	0.51
4	Cotton, hydrolyzed by *N* HCl	1.20×10^{-3}	0.72
5	Cotton, hypochlorite bleached at pH 6	0.65×10^{-3}	0.37
6	Cotton, hypochlorite bleached at pH 6	1.05×10^{-3}	0.52
7	Cotton, hypochlorite bleached at pH 6	2.70×10^{-3}	1.35
8	Cotton, hypochlorite bleached at pH 6	4.55×10^{-3}	2.51
9	Cotton, oxidized in 0.01 *M* KIO_4	0.51×10^{-4}	0.58
10	Cotton, oxidized in 0.01 *M* KIO_4	1.39×10^{-3}	1.42
11	Cotton, oxidized in 0.01 *M* KIO_4	2.36×10^{-3}	2.72
12	Cotton, oxidized in 0.01 *M* KIO_4	2.70×10^{-3}	2.90
13	Spruce sulfite, pulp No. 2	1.35×10^{-3}	0.80
14	Spruce sulfite, pulp No. 2, purified by alkali boil	0.42×10^{-3}	0.24
15	Spruce sulfite bleached with hypochlorite in 5.5 *N* NaOH	1.53×10^{-3}	0.90

at constant pressure (see Figures 2, 3, and 5), particularly that of the kiered cotton alkali cellulose, suggest that these reactions are radical chain processes. The following provisional scheme is therefore postulated:

$$\text{CELL—CHO (I)} + O_2 \rightarrow \text{CELL—CO— (II)} + \text{—}HO_2\ \text{(II)} \quad \text{(i)}$$

$$\text{CELL—CO— (II)} + O_2 \rightarrow \text{CELL·CO·(OO—) (IV)} \quad \text{(ii)}$$

$$\text{CELL—CO(O—O—) (IV)} + \text{CELL·H (V)} \rightarrow \text{CELL—CO(OOH) (VI)} + \text{CELL— (VII)} \quad \text{(iii)}$$

$$\text{CELL— (VII)} + O_2 \rightarrow \text{CELL—O—O— (VIII)} \quad \text{(iv)}$$

$$\text{CELL—O—O— (VIII)} + \text{CELL·H (V)} \rightarrow \text{CELL—O—OH (IX)} + \text{CELL— (VII)} \quad \text{(v)}$$

Reactions (i), (ii), and (iii) represent the initiation of an autoxidation chain reaction in unmodified cellulose (V) by the initial reaction of molecular oxygen with an aldehydic reducing group. There is considerable evidence to suggest that the autoxidation of aldehydes begins by a dehydrogenation process and results in the production of peracids (*e.g.*, VI) by a chain reaction [27].

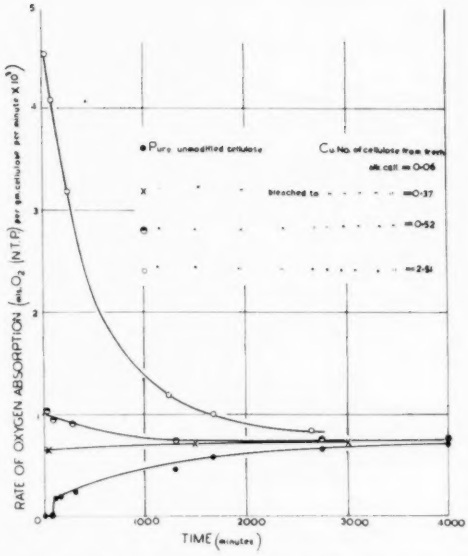


FIG. 5. *The effect of progressive hypochlorite bleaching (at pH 6) of pure cotton cellulose on the autoxidation characteristics of the derived alkali cellulose (at 25°C and* P_{O_2} *= 700 mm. Hg).*

Processes (iii), (iv), and (v) represent the extension of the chain reaction to unmodified cellulose, producing oxidation which may result in molecular fission. The chain autoxidation of unmodified cellulose may then proceed by alternation of reactions (iv) and (v). Chain-terminating reactions may include the usual radical associations. It is known, however, that carbohydrates and alcohols generally may be efficient inhibitors of chain reactions [27], so it is possible that in this case cellulose may be its own antioxidant, and hence the reaction chains may be relatively short.

The autocatalytic character of the autoxidation of alkali cellulose of low copper number indicates that some slow chain-branching reaction is occurring. This may well be similar to the process postulated for autocatalysis in olefine autoxidation [1, 19]:

$$\text{CELL—O—OH} \rightarrow \text{CELL—O—} + \text{—OH}, \quad \text{(vi)}$$

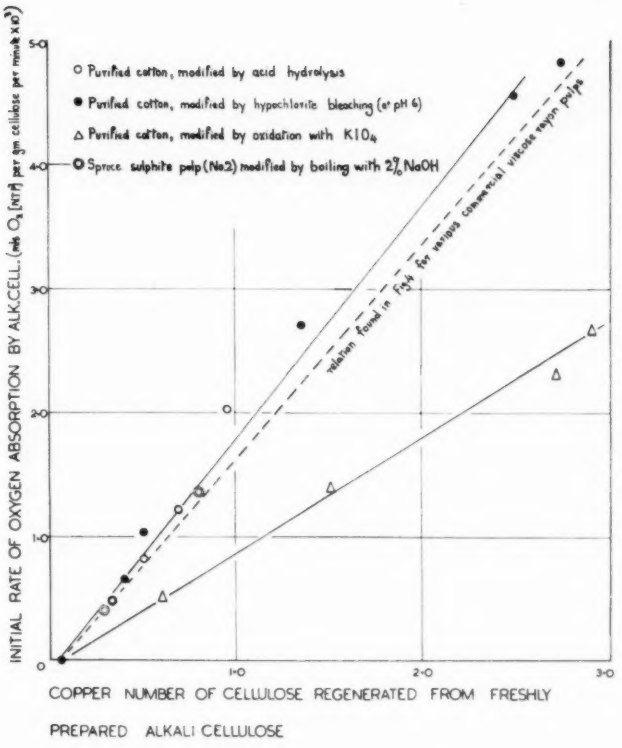

INITIAL RATE OF OXYGEN ABSORPTION BY ALK.CELL. (mls O_2 [N.T.P.] per gm cellulose per minute x 10^3)
COPPER NUMBER OF CELLULOSE REGENERATED FROM FRESHLY PREPARED ALKALI CELLULOSE
○ Purified cotton, modified by acid hydrolysis
● Purified cotton, modified by hypochlorite bleaching (at pH 6)
△ Purified cotton, modified by oxidation with KIO_4
⊙ Spruce sulphite pulp (No2) modified by boiling with 2% NaOH
relation found in Fig. 4 for various commercial viscose rayon pulps
0
1·0
2·0
3·0
4·0
5·0

FIG. 6. *Relation between initial rate of autoxidation of alkali celluloses, prepared from various modified celluloses, and copper number of derived celluloses (at 25°C and P_{O_2} = 700 mm. Hg).*

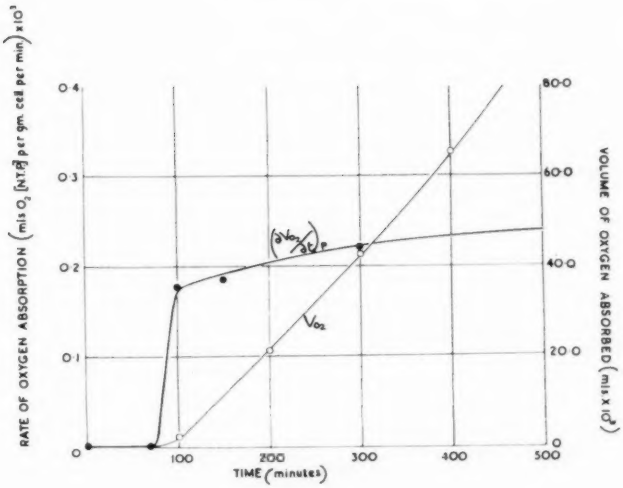


FIG. 7. *Induction period in the autoxidation of an alkali cellulose of low reducing value (from kiered cotton cellulose of Cu No. = 0.06).*

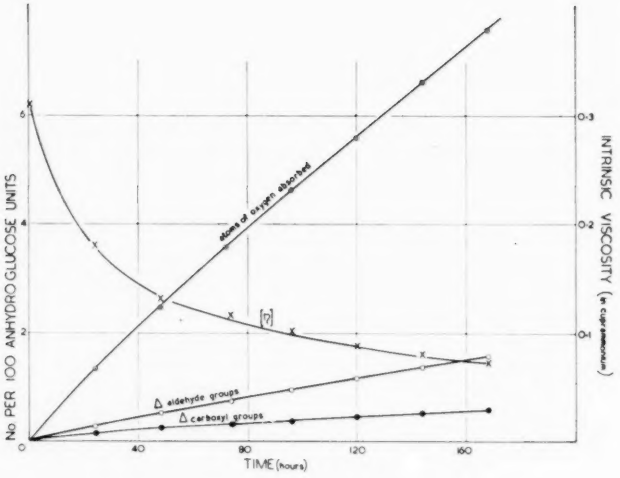


FIG. 8. *Changes in cellulose during autoxidation of alkali cellulose pulp No. 2 (Table I).*

occurring by thermal fission of the relatively weak O—O bond. It is possible that the reaction chain may also be propagated by dehydrogenations involving the —OH and perhaps the —OOH radicals.

Peroxide Formation

The process of autoxidation, as already discussed, is evidently likely to lead to peroxide formation. The production of peroxide during the autoxidation of alkali cellulose has been demonstrated by the present authors. Results are given in Figures 11 and 12.

According to Waters [27] hydroperoxides are readily hydrolyzed in alkaline solution:

$$R{-}OOH + H_2O \rightarrow R{\cdot}OH + H_2O_2. \quad \text{(vii)}$$

It has not been possible to decide, in this case, whether the peroxide estimated is present as a hydroperoxide of cellulose or as hydrogen peroxide. Measured peroxide concentrations have always been low and considerable variation is evident in the behavior of alkali celluloses prepared from different commercial cellulose pulps. It is shown (see Figure 12) that traces of various metals or their cations are capable of reducing the peroxide concentration almost to zero; indeed, no peroxide is detectable in an alkali cellulose which contains as little as 0.0005% of cobalt. Reference to Part II of this work [8] shows that metals which decrease peroxide formation include both metals which catalyze the autoxidation of alkali cellulose and those

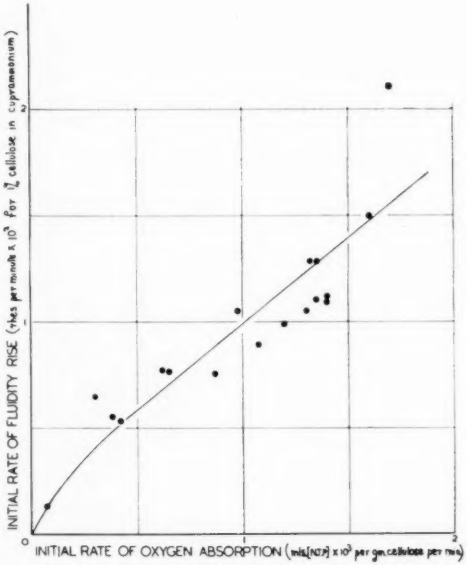


FIG. 9. *Relation between initial autoxidation rate and initial rate of rise of cuprammonium fluidity for various alkali celluloses (at 25°C in oxygen at ~ 700 mm. Hg).*

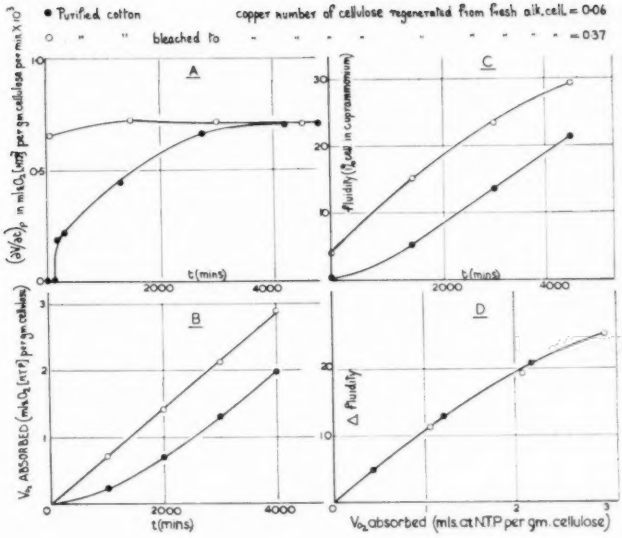

● Purified cotton
copper number of cellulose regenerated from fresh alk.cell. = 0·06
○ " " bleached to " " " " " " " = 0·37
A
B
C
D
t(mins)
Fluidity (Reid in Cuprammonium)
Δ Fluidity
V_O2 absorbed (mls. at NTP per gm. cellulose)

FIG. 10. *Relation between rates of autoxidation and fluidity change for alkali celluloses prepared from* (a) *purified cotton cellulose and* (b) *the same material after bleaching.*

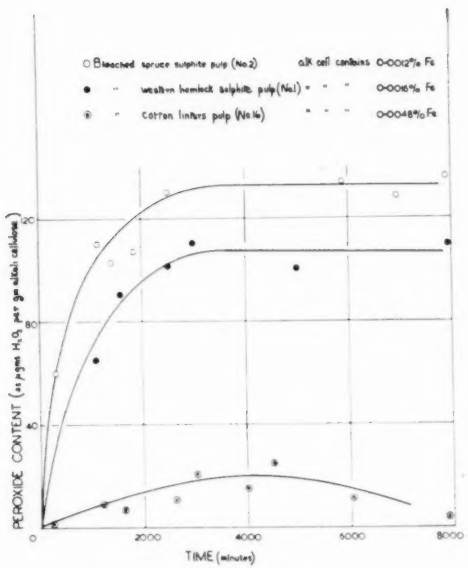

○ Bleached spruce sulphite pulp (No.2) alk cell contains 0·0012% Fe
● " western hemlock sulphite pulp (No.1) " " " 0·0016% Fe
⊙ " cotton linters pulp (No.14) " " " 0·0048% Fe
PEROXIDE CONTENT (as μgms H2O2 per gm alkali cellulose)
TIME (minutes)

FIG. 11. *Development of peroxide during autoxidation of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

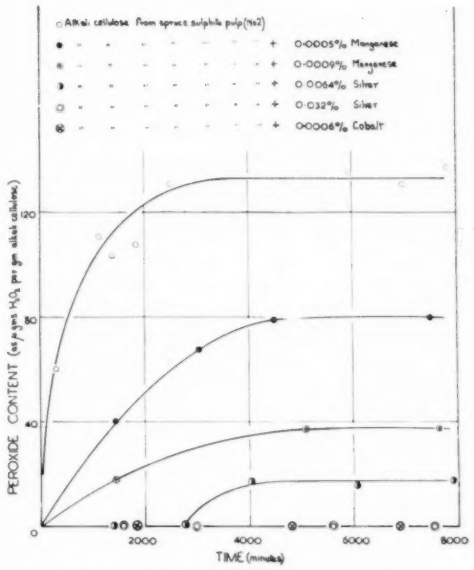

○ Alkali cellulose from spruce sulphite pulp (No2)
● " " " " " " + 0·0005% Manganese
⊙ " " " " " " + 0·0009% Manganese
◑ " " " " " " + 0·0064% Silver
○ " " " " " " + 0·032% Silver
⊗ " " " " " " + 0·0006% Cobalt
PEROXIDE CONTENT (as μgms H2O2 per gm alkali cellulose)
TIME (minutes)

FIG. 12. *Effect of various metals on development of peroxide during autoxidation of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

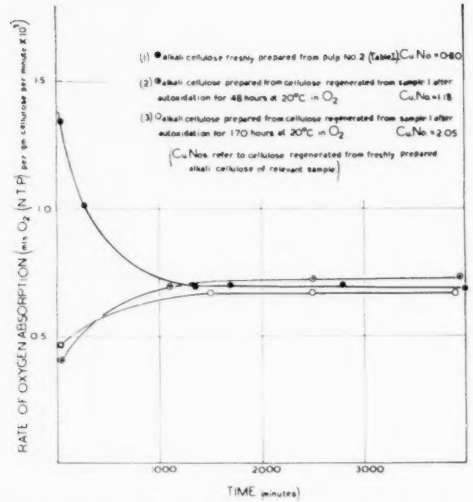

(1) ● alkali cellulose freshly prepared from pulp No. 2 (Table) Cu No. = 0.80
(2) ● alkali cellulose prepared from cellulose regenerated from sample 1 after autoxidation for 48 hours at 20°C. in O2 Cu No. = 1.18
(3) ○ alkali cellulose prepared from cellulose regenerated from sample 1 after autoxidation for 170 hours at 20°C. in O2 Cu No. = 2.05
(Cu Nos. refer to cellulose regenerated from freshly prepared alkali cellulose of relevant sample)
RATE OF OXYGEN ABSORPTION (cm. O2 (N.T.P.) per gm. cellulose per minute x 10)
1.5
1.0
0.5
1000
2000
3000
TIME (minutes)

FIG. 13. *The effect of alkaline autoxidation of cellulose on the autoxidation characteristics of the derived alkali cellulose (at 25°C and $P_{O_2} = 700$ mm. Hg).*

which behave as inhibitors. Catalysis of the main reaction is therefore not directly related to peroxide decomposition. It is likely, however, that the decomposition of both hydroperoxides and hydrogen peroxide by cations of transition metals which catalyze the autoxidation reaction may lead to the production of hydroxyl radicals [9, 12, 19], while their decomposition by silver oxide or metallic silver may take some other course which does not involve radical formation.

The considerable variations in peroxide concentration developed during the autoxidation of alkali-celluloses from various commercial pulps is almost certainly connected with their varying content of traces of catalytically active metals—particularly of iron (see Figure 11). The present theory suggests that the final steady autoxidation rate of alkali cellulose is a reflection of a dynamic equilibrium in the chain reaction (see below), and it is possible that the observed small variations in this steady rate, as between one commercial pulp and another (Figures 2 and 3), are also due to variations in catalytically active metal content.

Hydrogen peroxide may, as shown above, be produced by hydrolysis of hydroperoxides; it may, perhaps, also be produced by hydroxyl radical association. It should be noted that both this reaction and the hydrolysis of hydroperoxides to hydrogen peroxide reduce the possibilities of chain initiation and propagation processes.

The "Steady State" Reaction

Figures 2, 3, and 5 show that, irrespective of initial autoxidation rates, a large variety of alkali celluloses reach an almost identical steady rate after some time has elapsed, despite the fact that the reducing value of the alkali cellulose increases steadily with increasing autoxidation (see Figure 8). It is evident, therefore, that in this case, as in that of the initial rates of alkali celluloses from periodate-oxidized celluloses (see Figure 6), not all of the reducing groups present are functioning as reaction chain initiators. The final steady state must be one in which the rate of formation of active, chain-initiating, reducing groups by oxidation equals their rate of destruction by further oxidation and in which an increasing concentration of non-active reducing groups is built up. Figure 13 emphasizes this point. The upper curve of Figure 13 represents the variation of autoxidation rate with time of an alkali cellulose. At increasing times during this autoxidation, samples of cellulose were regenerated from the alkali cellulose by acidification with acetic acid, followed by washing and drying. They were then reconverted into alkali cellulose and their autoxidation rate-time curves were redetermined. The results show that initial rates of autoxidation are then actually below the steady rate and substantially independent of copper number, despite the fact that this may have a much greater value than that corresponding to the fast initial rate of the original alkali cellulose.

The initial low rates of autoxidation, characteristic of these alkali celluloses prepared from cellulose regenerated from an already considerably autoxidized alkali cellulose, are presumably due to some loss during the regeneration and re-steeping of the cellulose of reducing material of low molecular weight, which is capable of initiating the reaction. Despite this, however, the copper number of the residue is high.

Nature of the Autoxidation-Initiating Reducing Group

Strict analysis of these results in order to determine the precise structure in modified cellulose

which is responsible for autoxidation chain initiation is rendered difficult by a lack of basic knowledge of the chemistry of cellulose modification by even such classical reagents as hypochlorite.

Only in the cases of acid hydrolysis and of periodate oxidation may the resultant structure be described with any certainty. Even here, however, it is certain that alkali, of the concentration present in alkali cellulose, produces considerable further structural modifications. Thus, while acid hydrolysis of a pure undegraded cellulose produces a material the reducing power of which is confined to aldehyde groups on C_1 of the reducing end of the cellulose molecule, reversible keto-enol transformations likely to occur in the presence of alkali will allow the carbonyl group to migrate either to C_2 or to C_3. The structure of hypochlorite-bleached or periodate-oxidized cellulose may show similar mobility under alkaline conditions. It does not, therefore, seem possible to decide at this stage whether the whole of the reducing value of the cellulose derived from a given freshly prepared alkali cellulose is responsible for autoxidation chain initiation or, alternatively, whether this activity rests in a smaller quantity of some, at present unspecified, reducing structure. There are, however, some relevant facts which should not be overlooked. Thus, for a given reducing value of the regenerated cellulose, the initial autoxidation rate of alkali cellulose is almost exactly double that from a periodate-modified material (see Figure 6). It is significant, moreover, that the addition of glucose itself, as shown in the next paper of this series [8], does not induce autoxidation of alkali cellulose, although glucose is readily autoxidizable in the presence of alkali.

TABLE III. EFFECT OF TEMPERATURE ON THE "STEADY" REACTION VELOCITY (AT P_{O_2} = 300 MM. HG)

Temperature (°C)	$10^3/T°k$	Velocity coefficient (k) ml. O_2 (n.t.p.)/g. cell./min.	$\log_{10} k$
5	3.60	3.66×10^{-5}	−4.44
15	3.47	1.40×10^{-4}	−3.85
23	3.38	3.60×10^{-4}	−3.44
25	3.36	4.16×10^{-4}	−3.38
30	3.30	9.0×10^{-4}	−3.05
50	3.10	6.6×10^{-3}	−2.18
55	3.05	1.1×10^{-2}	−1.96
60	3.00	1.8×10^{-2}	−1.80
65	2.96	2.8×10^{-2}	−1.55
70	2.92	3.9×10^{-2}	−1.41
75	2.87	7.2×10^{-2}	−1.14
80	2.83	1.25×10^{-1}	−0.90

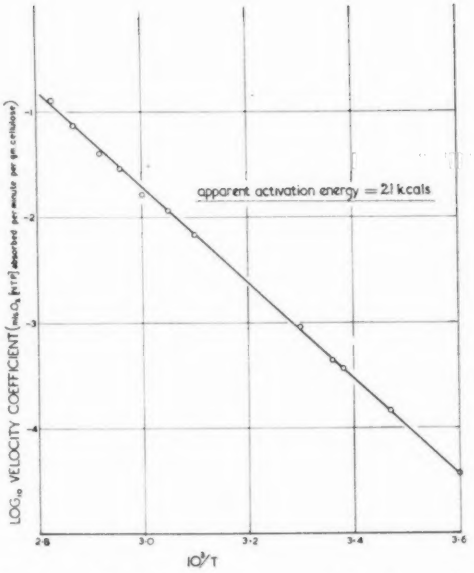


FIG. 14. *Effect of temperature on velocity of autoxidation of alkali cellulose* (P_{O_2} = *300 mm. Hg*).

Clearly, much more critical work is required in this field. At the present it is felt that the initial autoxidation rate of the derived alkali cellulose may be an additional, useful, measurable property of modified cellulose.

Effect of Temperature on Autoxidation Rate

The rapid variation of reaction rate with time in the early stages of alkali cellulose autoxidation introduces difficulties into the quantitative study of the effect of other variables on the reaction because during such study an appreciable amount of reaction must occur, together with its associated rate change. In studying the effect of temperature and other variables it has been found necessary to allow reaction to proceed until the "steady" rate under the given conditions is reached, after an oxygen absorption of approximately 1 ml. (n.t.p.) per g. cellulose, before making the required rate measurement. This could then be done rapidly, using the absorptiometer shown in Figure 1, with a minimum of oxygen consumption and, hence, of rate variation due to the above cause, during the measurement. Table III and Figure 14 record the variation of

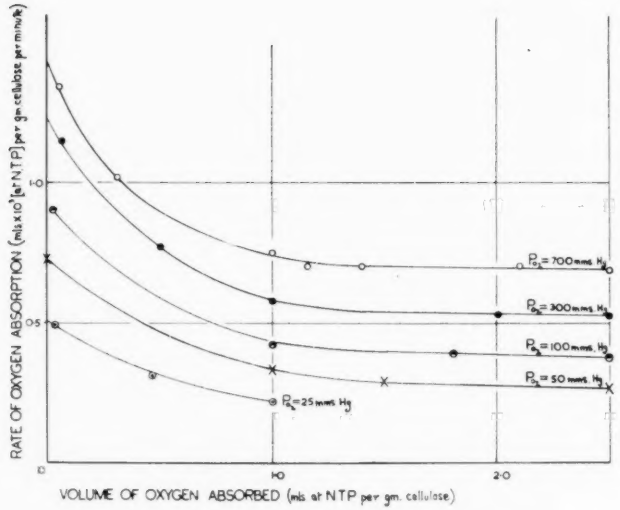

RATE OF OXYGEN ABSORPTION (mls x10³ [at N.T.P.] per gm cellulose per min/g)
1·0
0·5
0
1·0
2·0
VOLUME OF OXYGEN ABSORBED (mls at N.T.P per gm. cellulose)
P$_{O_2}$= 700 mms. Hg
P$_{O_2}$= 300 mms. Hg
P$_{O_2}$= 100 mms. Hg
P$_{O_2}$= 50 mms. Hg
P$_{O_2}$= 25 mms. Hg

FIG. 15. *The effect of oxygen pressure on the course of alkali cellulose autoxidation at 25°C.*

the "steady" reaction velocity with temperature over the range of 5°C to 80°C for alkali cellulose (of the composition defined as normal) prepared from the spruce sulfite cellulose pulp No. 2. A separate sample was, of course, used for the measurement at each temperature. The activation energy of the reaction is constant over this temperature range and amounts to approximately 21 kg. cals. per mole. This corresponds to nearly a three-fold increase in reaction rate for a 10°C rise at room temperature.

Effect of Oxygen Pressure on Autoxidation Rate

Figure 15 shows how the curve relating reaction rate to amount of reaction at constant oxygen pressure is displaced by changes of oxygen pressure.

The results given in Figure 16*a* were obtained as follows. A sample of alkali cellulose in the absorptiometer was allowed to absorb 1 ml. of oxygen per g. of cellulose and so reach a state at which the rate of oxygen absorption changed slowly with further reaction. Oxygen pressure was then reduced in stages by pumping, and reaction rate was measured over 30-minute periods at a succession of oxygen pressures down to 10 mm. Hg. This procedure gave the response of reaction rate to oxygen pressure only, as the amount of oxygen absorbed during the whole run was small. When oxygen pressure was changed suddenly there was a short but recognizable time lag before the reaction rate settled down to the steady value corresponding to the new pressure. Such behavior might be expected in a chain reaction.

As will be seen in the ensuing discussion, it was necessary to evaluate the way in which the response

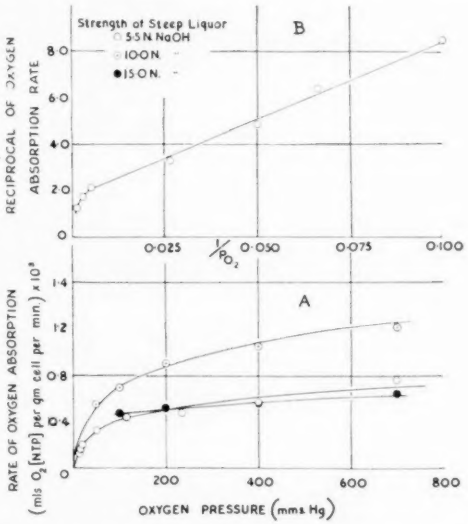


FIG. 16. *The effect of oxygen pressure on the rate of autoxidation of alkali cellulose at 25°C.*

TABLE IV. RELATIONSHIP BETWEEN ALKALI CELLULOSE COMPOSITION, OXYGEN PRESSURE, AND AUTOXIDATION RATE (VELOCITY COEFFICIENT AS ML. O_2 (N.T.P.)/G. CELL./MIN. $\times 10^3$)

Concentration of steeping solution (mols./l.)	5.5		10		15	
Composition of alk. cell.:						
% cellulose	30		33.0		32.3	
% sodium hydroxide	15		22.7		29.5	
% water	55		44.3		38.2	
	P_{O_2} (mm. Hg)	Velocity coefficient	P_{O_2} (mm. Hg)	Velocity coefficient	P_{O_2} (mm. Hg)	Velocity coefficient
	10	0.12	50	0.55		
	15	0.16	100	0.70	100	0.47
	20	0.21	200	0.91	200	0.51
	50	0.33	400	1.06	400	0.56
	124	0.43	700	1.22	700	0.65
	235	0.48				
	400	0.57				
	700	0.77				

of reaction rate to oxygen pressure varied with the concentration of sodium hydroxide in the steeping solution used to prepare the alkali cellulose. Table IV and Figure 16*a* record the results obtained when the sodium hydroxide concentration was 5.5*M*, 10*M*, and 15*M*. In Figure 16*b* the results for the first of these series—that of the normal alkali cellulose—are analyzed in more detail, and it is evident that, over the pressure range 10–235 mm. Hg at least,

$$-d[O_2]/dt = \alpha P_{O_2}(1 + \beta P_{O_2}). \qquad \text{(viii)}$$

It is possible that this relation holds up to even greater pressures, but further data, preferably at oxygen pressures higher than atmospheric, would be required to explore this point.

Oxygen pressures of below 20 mm. Hg are measurable with decreasing accuracy on account of the relatively high water-vapor pressure of alkali cellulose. Down to 20 mm. Hg, however, the reaction order with respect to oxygen pressure is well below unity. In the pressure range 50–700 mm. Hg, sodium hydroxide concentration has remarkably little effect upon the response of the reaction rate to oxygen pressure.

A similar relative insensitivity of reaction rate to oxygen pressure has been observed for many other autoxidation processes [27]. For ethyl linoleate autoxidation, Bolland and Gee [1] obtained a rate expression similar to equation (viii) and showed that it could be derived theoretically by analysis of the kinetic equations postulated by them for this radical chain reaction. G. V. Schulz [21] studied the autoxidation of cellulose dissolved in cuprammonium hydroxide solution and, making measurements with air and with oxygen at atmospheric pressure, found the depolymerization rate proportional to the square root of oxygen pressure. This result was used as the basis of a theory of the reaction mechanism. Unpublished results of the present authors have shown that there is a small but definite increasing dependence of reaction rate upon oxygen pressure as temperature rises from 5°C to 80°C, and it is felt that, while at oxygen pressures above 10 mm. Hg the pressure dependence is to be explained mainly in terms of the kinetics of a radical chain reaction, oxygen availability is a second-order effect important at low pressures, at high temperatures, and possibly under other conditions—*e.g.*, with catalysts, where the reaction rate may be high.

Effect of Alkali Cellulose Composition on Its Autoxidation Rate

A range of alkali celluloses was prepared from the pulp No. 2 (Table I) using sodium hydroxide steeping solutions of concentrations varying from 2*M* to 15*M* at 25°C. At each steeping concentration two samples were prepared, one pressed at 42 and the other at 377 lb. per square inch. Each sample was disintegrated in a small stainless-steel pfleiderer for 10 minutes at 25°C. and its rate of autoxidation was measured at 40° C and 500 mm. Hg pressure of oxygen. Results are given in Table V and Figure 17. As found by Davidson [5], autoxi-

TABLE V. EFFECT OF STEEPING AND PRESSING CONDITIONS ON ALKALI CELLULOSE COMPOSITION AND "STEADY" RATE OF AUTOXIDATION AT 40°C AT P_{O_2} = 500 MM. HG

Concentration of sodium hydroxide in steeping solution mols./l.	Applied pressure (lb. per sq. in.)	Alkali cellulose composition			Rate of oxygen absorption (ml. O_2 (n.t.p.) per g. cell. / min. $\times 10^4$)
		% cellulose	% sodium hydroxide	% water	
2.03	42	38.5	3.1	58.4	1.2
2.77	42	31.1	7.9	61.0	1.8
3.55	42	22.1	10.7	67.2	2.6
4.37	42	22.7	12.9	64.4	3.5
5.20	42	22.2	15.0	62.8	—
6.10	42	24.1	16.3	59.6	5.3
7.98	42	23.3	19.9	56.8	6.2
9.96	42	23.6	21.8	54.6	6.4
14.3	42	24.0	36.0	40.0	2.6
2.03	377	45.0	5.4	49.6	1.2
2.77	377	36.8	8.0	55.2	1.8
3.55	377	31.0	10.6	58.4	2.6
4.37	377	31.4	12.6	56.0	3.5
5.20	377	32.0	14.4	53.6	—
6.10	377	32.0	16.0	52.0	5.3
7.98	377	31.4	19.0	49.6	6.2
9.96	377	31.0	21.8	47.2	6.4
14.30	377	30.2	34.2	35.6	5.0

dation velocity increases progressively with increasing sodium hydroxide concentration, passes through a maximum when the steeping solution has a concentration in the region of 10*M* sodium hydroxide, and then falls off with further increases in alkali concentration. Figure 17 shows that, at a sodium hydroxide concentration below 10*M*, the autoxidation rate is independent of the pressure applied to express the sodium hydroxide solution during alkali cellulose manufacture and, hence, of the cellulose content of the alkali cellulose. In the region beyond the maximum rate, however, the rate is strongly

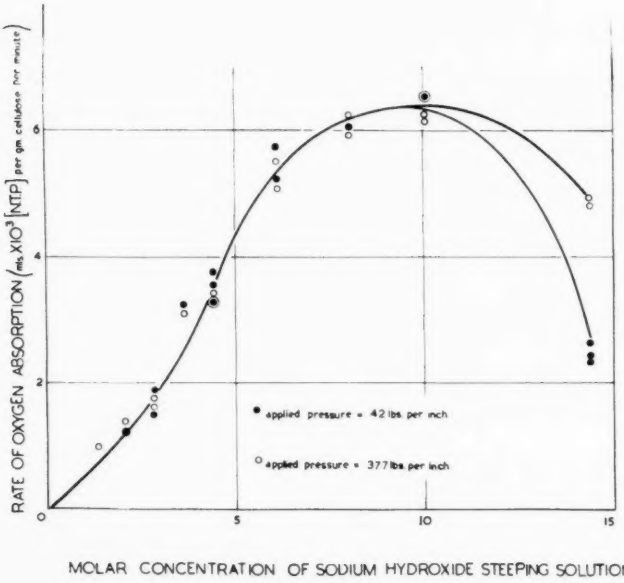


FIG. 17. *Effect of applied pressure and concentration of sodium hydroxide steeping solution during manufacture of alkali cellulose on steady rate of autoxidation at 40°C and* $P_{O_2} = 500$ *mm. Hg.*

dependent upon this applied pressure. Observation suggests that this latter effect is probably a function of the physical state of the material, since the samples on which the low rate was recorded were compressed together into large damp lumps by the grinding operation, while all other samples were opened so that they were in a loose fibrous condition. A further series of experiments was carried out to determine the effect of concentration of sodium hydroxide on the manner in which autoxidation rate varied with time at constant oxygen pressure (700 mm.Hg) at 25°C. The results are given in Figure 18, while Table VI records the composition of the various alkali celluloses. Under these conditions the maximum reaction rate is associated with a steeping solution concentration in the region of 12.5*M*. Changing alkali concentration affects both the initial and the subsequent reaction rates. The highest rates are associated with some degree of autocatalysis.

TABLE VI. COMPOSITIONS OF ALKALI CELLULOSES, THE AUTOXIDATION CHARACTERISTICS OF WHICH ARE GIVEN IN FIGURE 19

Concentration of sodium hydroxide in steeping solution (g. mols. per l.)	Alkali cellulose composition		
	% cellulose	% sodium hydroxide	% water
3	28.2	9.8	62.0
5.5	28.5	15.2	56.3
8	32.1	20.2	47.7
10	31.0	23.4	45.6
12.5	30.5	26.1	43.4
15	28.0	30.0	42.0
20	25.9	36.0	38.1

Discussion

A possible explanation of the shape of the curve in Figure 17 is that it is a composite result of two opposing factors—increasing sodium hydroxide concentration producing increasing cellulose reactivity, and simultaneously depressing oxygen solubility in the alkali cellulose. If this were so, then reaction rate would become increasingly sensitive to oxygen pressure as sodium hydroxide concentration increases and oxygen availability in the alkali cellulose becomes increasingly a rate-determining factor. (Reactions the rates of which are controlled by the diffusion of a reactant to the site of the reaction are generally first order with respect to the ambient concentration of this reactant.) The results given in Figure 16*a* clearly indicate that this does not, in fact, occur because reaction order with respect to oxygen pressure does not change appreciably on passing from 5.5*M* to 15*M* steeping concentration. It must be concluded that the maximum in the curve relating reaction rate to steeping concentration is due to some less obvious physical or chemical effect of the increasing concentration of alkali.

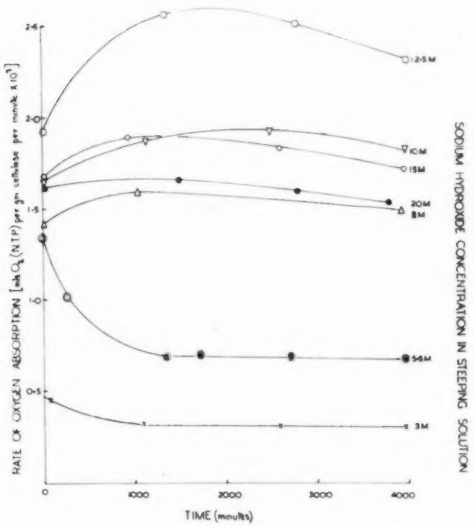


FIG. 18. *Effect of sodium hydroxide concentration on the autoxidation characteristics of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg.*

It seems unlikely that all regions of alkali-swollen cellulose will be equally susceptible to attack by molecular oxygen. The gradation of structural order from amorphous to crystalline, which is characteristic of unswollen cellulose, is apparently retained in alkali cellulose prepared at room temperature. This material shows an x-ray diffraction pattern which varies according to the concentration of sodium hydroxide and to the temperature of steeping, but which indicates that crystalline regions are present. These appear to be derived from the original cellulose crystallites and are swollen, containing presumably both sodium ions and water molecules in addition to cellulose. However, the intermolecular forces necessary to preserve such crystallinity against the strong swelling influence of alkali must restrict diffusion into the crystallites of oxygen molecules. In other words, oxygen should

be more soluble in the amorphous regions of alkali cellulose and consequently the greatest oxidative attack is to be expected there. Important also is the consideration that reaction-chain-initiating reducing groups, produced by oxidative or hydrolytic modification of the cellulose, will also occur predominantly in the amorphous portion of the original cellulose. It is here, therefore, that autoxidation of alkali cellulose will be initiated. Moreover, there is good reason to suppose that in the amorphous regions of swollen cellulose the cellulose chain segments possess considerable mobility, being restricted where they enter adjacent crystalline regions. The swollen amorphous region can be pictured as behaving at the molecular level as a "two-dimensional" solution. Since the propagation of a radical chain reaction requires a system of considerable mobility, there is additional reason for supposing that autoxidation in alkali cellulose will occur more rapidly in the mobile amorphous regions than in the rigid crystallites.

Figure 19 shows that while oxygen consumption proceeds almost linearly to values of more than 50 ml. oxygen (at n.t.p. per g. cellulose) the intrinsic viscosity of the cellulose falls rapidly at first and then much more slowly. Davidson [6] noted a similar effect in the action of aqueous strong acids upon cotton cellulose. It has been calculated that during such hydrolysis the intrinsic viscosity in cuprammonium rapidly approaches a value of approximately 0.069 and thereafter does not decrease significantly over a considerable period of time. Under similar conditions the spruce sulfite cellulose pulp used by us reached a limiting intrinsic viscosity of 0.062 during acid hydrolysis.

When the same pulp was degraded by autoxidation as alkali cellulose in oxygen at 25°C (see Figure 19) the rate of fall of degree of polymerization slowed down markedly when the intrinsic viscosity had fallen to 0.06 after 200 hours' reaction. There was, however, a further slow progressive depolymerization, and after 3,000 hours intrinsic viscosity had fallen to 0.02. It appears that in the case of alkali cellulose autoxidation proceeds rapidly in the amorphous regions, and that a slower attack on the crystalline regions also occurs. Over the range of reaction covered in Figure 19, the amount of insoluble cellulose recoverable by acidification and washing of the alkali cellulose decreased almost linearly with increasing time.

Calculation shows that approximately two molecules of oxygen were consumed in the over-all autoxidation process per anhydroglucose unit rendered water-soluble under the present experimental conditions. It is not suggested that this result has any theoretical significance.

The increasing reaction rate as steeping soda concentration rises from 0 to 10*M* bears little relation to the degree of swelling of the alkali cellulose. This point is brought out by the results given in Figure 17 and is emphasized by the fact that maximum unrestricted swelling occurs at a steeping soda concentration in the region of 3.6*M* at room temperature. It seems reasonable to suppose, therefore, that cellulose is rendered autoxidizable in alkali cellulose by reaction with alkali of some functional group, and that the equilibrium

$$\text{Cellulose} + \text{OH}^- \rightleftarrows \text{autoxidizable cellulose} \quad \text{(ix)}$$

is progressively displaced to the right with increasing concentration of sodium hydroxide in the steeping solution.

In accordance with the picture of the chain reaction which has already been given, this reaction of alkali may be either with the aldehyde reducing

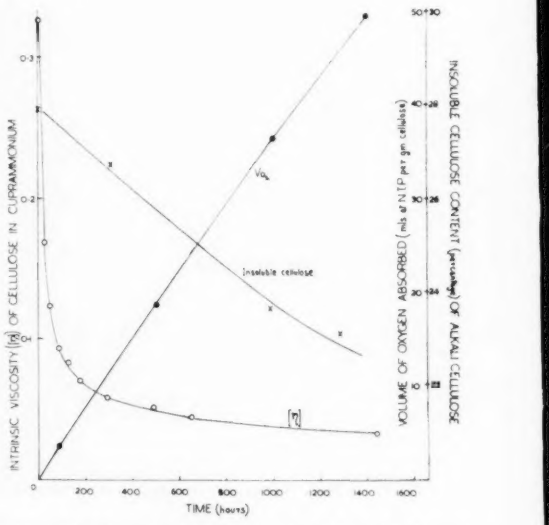


FIG. 19. *Oxygen absorption and cellulose depolymerization during prolonged autoxidation of alkali cellulose (at 25°C and 1 atmosphere pressure of oxygen).*

groups at which the radical chains are initiated by autoxidation or with the unmodified cellulose in which the reaction is propagated. It is evident that alkali influences the former structure, since a water-swollen aldehyde oxycellulose is quite stable to oxygen at room temperature in the absence of alkali, and the initial rate of alkali cellulose autoxidation increases progressively with increasing alkali concentration.

Enolization of aldehydes and ketones occurs generally in the presence of alkali and is a change which may be uniformly progressive over a considerable alkali concentration range. It is tempting to suppose, therefore, that the primary process of alkali cellulose autoxidation is the reaction of molecular oxygen with the enolic form of some reducing structure. Weissberger and others, in an interesting series of papers [13, 28, 29], have shown that the rate of autoxidation of many α-hydroxy ketones and similar compounds increases with increasing pH of the solution. The rate of autoxidation of benzoin bears the same relationship to hydroxyl ion concentration as does the rate of racemization of optically active benzoin, a process which can proceed only by enolization. Enolization of a terminal aldehyde group on cellulose yields the structure:

$$R{-}CH^{*}(OH){\cdot}C(OH){:}C\ H\ O^{-}.$$

The marked "allyl" hydrogen might be particularly labile and subject to removal by molecular oxygen—especially if the hydroxyl group on the same carbon atom were also ionized.

Indications of the effect of alkali concentration on the chain propagation reaction in the mass of unmodified cellulose are less definite. It is a matter of general observation that the autoxidation of alcohols and phenols is favored by alkaline conditions. Ionization of hydroxyl groups will lead to increased electron availability in those parts of the molecule adjacent to the negatively charged oxygen and will therefore facilitate oxidation. The presence of such an ionized oxygen on a hydrogen-carrying carbon atom will polarize strongly the C—H bond, thereby weakening it [25] and facilitating dehydrogenation. Neale's theory of the swelling of cellulose in alkaline solutions [17] requires ionization of hydroxyl by the process:

$$R{-}OH + OH^{-} \rightarrow RO^{-} + H_2O. \qquad (x)$$

His results give cellulose a pK of 13.7 for this reaction, presumably for dissociation of the first hydroxyl group of the anhydroglucose unit. In accordance with the dissociation of polybasic acids, the second and third dissociation constants are likely to be progressively lower and, accepting Neale's theory, the degree of ionization of unmodified cellulose should increase smoothly with increasing concentration of sodium hydroxide in the steeping solution.

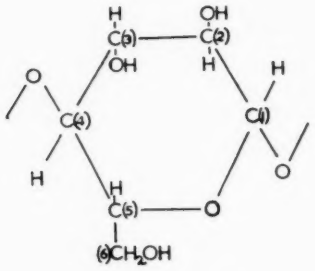
There is no obvious reason for supposing that the effect of alkali on either enolization of reducing structures or ionization of hydroxyl groups should pass through a maximum when the concentration of sodium hydroxide in the steeping solution is in the region of 10*M*–12.5*M*. Additionally, the results given in Figure 16*b* and discussed earlier suggest that this observed maximum in autoxidation rate at a particular alkali content is not explicable in terms of a decreasing oxygen solubility with increasing alkali concentration. It is possible, however, that increasing alkali concentration leads to an increased rate of hydrolysis of hydroperoxides to hydrogen peroxide (see reaction (vi)), thus reducing the importance of chain-branching processes. In this respect it is noteworthy that the highest reaction rates occurring at a steeping concentration of 10–12.5*M* NaOH are accompanied by some autocatalysis (see Figure 18), while at higher steeping concentrations the initial autoxidation rate is reduced and the rate falls off progressively with increasing time. It is possible also that increasing alkali content of the alkali cellulose and the accompanying decrease of water content lead to a decrease in the mobility of the system, increasing the physical resistance to the propagation in it of a chain reaction.

It has been suggested earlier in this paper that autoxidative attack on unmodified cellulose occurs at the carbon atom which carries an ionized hydroxyl group. There is, however, little direct evidence to show which of the three hydroxyl groups of the anhydroglucose unit is most likely to be ionized. Determination of the value of dissociation constants which lie in the region below 10^{-13} is extremely difficult.

McEwen [16] gives the following pK values for various alcohols: Methyl alcohol, pK = 16; ethyl, propyl, phenyl-ethyl alcohols, and benzhydrol, pK = 18. Landholt-Bornstein [14] gives pK = 12.7 for glucose and similar values for many other hexoses,

pK = 14.2 for ethylene glycol, and 13.8 for formaldehyde. If these results from different sources are comparable, it is evident that the dissociation constant of hydroxyl groups in an α-glycol structure is greater than that of primary alcohol groups, and it seems likely, therefore, that in alkali cellulose hydroxyl group ionization will be greatest at C_2 or C_3 and lowest in the primary alcohol at C_6. The chemical structure of the gluco-pyranose ring suggests that the strongest hydroxyl group is that on C_2, because this carbon atom is bonded to C_1 with two oxygen atoms attached and C_3 with one oxygen atom attached. The next strongest hydroxyl group is that on C_3, which is bonded to C_2 and C_4, each with one oxygen atom attached [20].

It is likely, therefore, that in the autoxidation chain reaction in alkali cellulose radical dehydrogenation will take place mostly at C_2, to a lesser extent at C_3, and least of all at C_6—*i.e.*, proportionally to the extent to which the attached hydroxyl groups are ionized. It must be admitted, however, that dehydrogenation by free radicals may not be precluded at any of the 6 carbon atoms of the anhydroglucose unit, and that such attack, at any site other than C_6, is likely to lead to degradation of the cellulose molecule.



Anhydroglucose unit.

The picture of alkali cellulose autoxidation suggested by these results is one of a complex reaction. The process is initiated at alkali-modified reducing groups in the cellulose and proceeds: (1) by a radical chain mechanism in which unmodified cellulose is oxidized, primarily by dehydrogenation; (2) by the hydrolysis of hydroperoxides to hydrogen peroxide and the subsequent oxidation of cellulose by the hydrogen peroxide so formed.

The next paper of the series [8] will give studies of the effect of catalysts and inhibitors on the reaction.

Experimental Procedure

1. Preparation of Alkali Cellulose

Except in the case of the work described in the discussion section, alkali cellulose composition was maintained at that normally employed in the manufacture of viscose rayon—*i.e.*, approximately 30% cellulose, 15% sodium hydroxide, and 55% water. It was prepared by steeping air-dry cellulosic material, either as commercial sheeted pulp cut to 3 in. × 4 in. or as loose fiber, at 25°C for 1 hour in 5.5*N* sodium hydroxide solution. This latter material was made up from laboratory reagent-grade sodium hydroxide pellets and distilled water. After removal from the steeping solution, sheeted material was pressed directly between stainless-steel plates in a small hand press to approximately three times its original air-dry weight. Cellulose steeped as loose fiber was filtered with suction before a similar pressing operation. In all cases the unsuitable "wet edges" were discarded, and after 5 minutes' mechanical disintegration in a small stainless-steel pfleiderer the alkali cellulose was transferred to the absorption vessel. In some experiments, where it was essential to measure the initial autoxidation rate as soon as possible after alkali cellulose manufacture, mechanical disintegration was dispensed with, since it was found that such treatment had no effect on autoxidation rate but merely ensured that various samples taken from the batch were thoroughly representative of the whole.

2. Measurement of the Rate of Oxygen Absorption by Alkali Cellulose

Measurements of oxygen absorption were carried out in the apparatus (Figure 1), which was constructed of Pyrex glass throughout. The tubular reaction vessel *A* held approximately 30 g. of alkali cellulose and had a total volume of 60 ml. With taps T_1 and T_2 open, it was connected to the large manostat *B*, of 4 liters' capacity. When the apparatus was initially filled with oxygen at a pressure of 700 mm. Hg an absorption of 0.2 millimols (4.5 ml. at n.t.p.) of oxygen per g. of cellulose resulted in an over-all pressure drop of only 1%. For the purposes of the present study, such an absorption represents a considerable amount of reaction, and constant pressure conditions may therefore be taken as established. The rate of oxygen absorption was followed at suitable intervals by closing tap T_2 and then measuring,

by means of a cathetometer situated outside the thermostat, the rate of movement of manometric liquid (dibutyl phthalate) in the differential manometer C. The cross-sectional area of the manometer tube was approximately 0.017 sq. cm. It may be shown that:

$$\left(\frac{\partial V}{\partial t}\right)_P = \left[1 + \frac{PA\rho\mathrm{Hg}}{20\rho\mathrm{DBP}}\left(\frac{1}{V} + \frac{1}{V''}\right)\right] \times \frac{\rho\mathrm{DBP}\ V \times 273}{760\rho\mathrm{Hg}\ W \times 298}\left(\frac{dh}{dt}\right)\mathrm{obs.},$$

where

$\left(\frac{\partial V}{\partial t}\right)_P$ = rate of oxygen absorption in ml. O_2 (n.t.p.) per g. cell./min.,
$\frac{dh}{dt}$ = measured rate of rise of dibutyl phthalate in C in mm./min.,
A = area of cross section of manometer C in sq. cm.,
V = dead space in ml. on reaction-vessel side of manometer C,
V'' = dead space in ml. on manostat side of manometer C,
P = oxygen pressure in apparatus in mm. Hg,
$\rho\mathrm{Hg}$ = density of mercury,
$\rho\mathrm{DBP}$ = density of dibutyl phthalate,
W = weight of cellulose in reaction vessel.

The whole apparatus, with the exception of the mercury manometer D, was immersed in a plate-glass-fronted water thermostat where temperature was controllable to ± 0.02°C at a point in the range 0°–40° C and rather less accurately at higher temperatures up to 80° C. The mercury manometer, which was of barometric height, was wound with resistance wire and could be heated as required to prevent condensation of water in it during experiments at elevated temperatures.

At the beginning of an experiment, the alkali cellulose sample was placed in reaction vessel A, and the whole apparatus was evacuated through the tap T_2 down to the vapor pressure of the alkali cellulose. Oxygen from a storage vessel in the same thermostat was then admitted to the required pressure. This oxygen had been stored over water. Preliminary experiments showed that the establishment of water-vapor equilibrium in the apparatus occurred rapidly and did not interfere with the kinetic measurements. When the reaction was to be carried out at an elevated temperature, the reaction vessel was swung clear of the thermostat during evacuation by rotation around the conical ground joint E. This prevented undue change in alkali cellulose composition due to loss of moisture. The reaction vessel was then lowered into the thermostat and allowed to reach temperature equilibrium before oxygen was admitted. The height of the manometer C was measured during an experimental run with a millimeter scale at suitable time intervals until a pressure difference of 20–50 mm. dibutyl phthalate was established. The plot of pressure difference against time under these conditions was accurately linear and its slope gave the "instantaneous" value of dh/dt. Total amounts of oxygen absorbed from the start of the reaction to a particular time were determined by graphical integration of the rates of absorption against time curves.

3. Determination of Cuprammonium Fluidity and of the Intrinsic Viscosity of Cellulose in Cuprammonium

Cuprammonium fluidity was determined for 1% solutions of cellulose by the method of Clibbens and Geake [4], as described in the "Viscosity of Cellulose Solutions," a Fabrics Research Committee report of the D.S.I.R. (1932). Intrinsic viscosities were calculated from such measurements by means of the Philippoff equation:

$$[\eta] = 8(\eta_{\mathrm{rel}}^{1/8} - 1)/c,$$

where c is in g. per liter.

4. Copper Numbers

Copper numbers were measured by the method of Clibbens and Geake [3].

5. Carboxyl Group Content

Carboxyl-group content was determined by the titration method of Neale and Stringfellow [18] on cellulose samples which had been steeped in dilute HCl and then subjected to electrodialysis for 24 hours, with a mean potential gradient of 10 volts per cm.

6. Peroxide Content of Alkali Cellulose

Two g. of the sample were added to 100 ml. of $2N$ sulfuric acid containing 0.1 g. of potassium iodide and 0.2 g. of ammonium molybdate. After standing in a dark place for 5 minutes, the liberated iodine was titrated rapidly with $N/500$ thiosulfate solution.

Acknowledgment

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Pore-Size Distribution in Textiles

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THE APPLICATION of various permeability tests to textiles and textile materials has been a practice in the industry for a number of years, and the determinations of densities and total porosities have long been subjects of interest in this field. Sieminski and Hotte [13] have pointed out that the distinction between the terms *porosity* and *permeability* has not at all times been appreciated. Porosity of a textile fabric pertains to the total volume of void space contained within its boundaries, whereas permeability refers to the accessibility of the void space to the flow of a gas or a liquid. Porosity is usually defined as the ratio of the void space to the total volume encompassed by the boundaries of the material. Permeability is an empirical value, usually expressed as a rate of flow of some liquid or gas per unit area of fabric, and is a function of, among other variables, the differential pressure. These two properties of a fabric are thus quite different, and the relationship that exists between them is likely to be complex.

The total porosity of a fabric can be visualized as having three components: (*a*) the intrafiber porosity, or the void space contained within the walls of the fibers themselves; (*b*) the interfiber porosity, or the void space contained between the fibers in the yarn; and (*c*) the interyarn porosity, or the void volume contributed by the interstices between the yarns. That part of the total porosity which is available to fluid flow has been called the "effective porosity" [13] and is largely a function of the interyarn and interfiber components. The total interfiber and interyarn porosity is, of course, in turn dependent upon such variable construction features as fiber "fineness" and shape, type of weave, number of yarns per inch, and yarn twist.

Various methods of determining the "effective porosity" of porous materials have been developed, mainly in the field of petroleum technology, some of which have been applied to textile materials. The method of Barnes [1] is based on the measurement of the weight of liquid required to fill the pore system of the material. The Washburn-Bunting [17] method measures the volume of air trapped in the open pore system of the sample when it is immersed in mercury at atmospheric pressure. The Russell volumeter method [2, 5, 11] measures the volume of the specific substance of the sample by immersion in a suitable liquid, but the total bulk volume of the sample must be determined by some other method in order to obtain the void volume. The Melcher-Nutting [7, 8, 9] method is essentially a pycnometric determination of the apparent density of the bulk sample previously coated with some material such as paraffin (correction being applied for the volume of the coating material), followed by a determination of the density of the specific substance of the sample. In the gravimetric method, which has been applied to fabrics [6, 12, 14, 15], the bulk volume of the sample is calculated from the dimensions (the thickness of the fabric being the most uncertain of these measurements), and the volume of the specific substance of the sample is calculated from its weight and density. The value of the density used is usually that of the fiber. In the Boyle's Law method [3] a gas is expanded from a vessel of known capacity containing the sample into a second vessel of known capacity, and the temperature and pressure before and after expansion are determined. This yields the volume of the specific substance of the sample. From a determination of the bulk volume by some other means the effective pore volume can then be calculated.

The foregoing methods of pore-volume measure-

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ment yield, in varying degrees, integrated values for the void volume contained within the sample. "Effective porosity" is involved because all the methods mentioned above, with the exception of the gravimetric method, depend upon the entry of a fluid medium at low pressure into the pores of the sample. No insight is gained, however, into the distribution of this volume according to pore sizes. It would seem that some knowledge of the manner in which this pore volume is distributed in pores of various sizes would be essential to a proper evaluation of porosity and of its significance in determining other fabric properties such as permeability, swelling (self-sealing) capacity, and perhaps even moisture sorption.

The present work represents an application to textile materials of the mercury-intrusion method described by Ritter and Drake [4, 10] and used by them for the determination of pore-size distribution of such materials as fritted glass, activated clay, porous plate, and diatomaceous earth. Their method is based on the principle pointed out by Washburn [16] that surface tension opposes the entry of any nonwetting liquid (any liquid having an angle of contact with the surface of the material greater than 90°) into a pore and that this opposition may be overcome by external pressure. Assuming circularity of pore cross section and constancy of contact angle, it can be shown [16] that the pressure, p, required to force a liquid into a pore of radius r is given by the equation

$$pr = -2\sigma \cos\theta, \qquad (1)$$

where σ is the surface tension of the liquid and θ is the contact angle it makes with the internal surface of the pore. Thus, pores of radius r are in equilibrium with the entering liquid at the pressure p, or, in other words, all pores whose radii are equal to or greater than r will have been filled at the pressure p. When a rigid porous material is immersed in such a liquid and subjected to continuously increasing pressure, a pressuring curve characteristic of that material is obtained by measuring the total cumulative volume of liquid forced into the pore system for each pressure. In the words of Ritter and Drake, "a given pore-size distribution gives rise to a unique pressuring curve; and, conversely, a given pressuring curve affords a unique determination of the pore-size distribution." Experimentally, the problem reduces to the dilatometric measurement of the total cumulative volume, ΔV, of liquid (mercury) forced into the pores of the material at each successive pressure as the pressure on the system is increased stepwise.

The derivation by Ritter and Drake of the distribution function for pore size, $D(r)$, is based on the fact that the volume of liquid entering the pores of the material is a function of the differential radius of the pores filled as the pressure is increased. The equation for the distribution function is

$$D(r) = \frac{p}{r}\frac{d(\Delta V)}{dp}, \qquad (2)$$

where r is the radius of the pores in equilibrium at pressure p (calculated from equation (1)) and $\frac{d(\Delta V)}{dp}$ is the slope of the pressuring curve at the pressure p, this slope being determined by graphical differentiation of the pressuring curve.

Sources of Error

The assumption regarding the circularity of cross section of the pores of the material is felt to be the largest source of error. For noncircular cross sections the ratio of circumference to cross-sectional area will no longer be $2/r$, and the effect will be to change the calculated radii. But it must be assumed for a series of similar materials, such as textile fabrics of various constructions, that this departure from circularity may be regarded as a constant factor throughout the series; then the relative positions of the distributions of the various members of the series may be considered unchanged, and intercomparison of the distributions in no way invalidated.

Similarly, an error in the contact angle would have the effect of shifting the derived distributions on the radius axis, but if the error is the same for all the fabrics studied, the intercomparison of the distribution curves again would still be valid. Throughout this investigation it is assumed that the value of the contact angle for mercury is 140°, the average value found by Ritter and Drake [10] between mercury and a number of substances.

The nonrigidity of the pore system of a material such as a fabric or a fiber can conceivably lead to a compression factor in the pressuring curve—that is, the pore system might be partially collapsed before being filled with the liquid. Thus, the pressuring curve would not exclusively represent the equilibrium between surface tension and external pressure that

is called for in the theory. In an open pore system with comparatively few constrictions such an error would be relatively unimportant, but in a system with a large number of what Ritter and Drake refer to as "ink-bottle" pores it might be very significant, particularly where the substance forming the pore system is nonrigid. This effect will be referred to later in the discussion of the high-pressure work on fibers. It can be seen that in a cotton fiber possessing a relatively large internal cavity or lumen, which is not easily accessible, such a compressibility could be an even larger factor than the flow of the liquid into the pores and would have a greater influence on the shape of the pressuring curve. The more open pore system of a fabric, on the other hand, is assumed not to be appreciably distorted under the relatively low pressures required to determine the distribution.

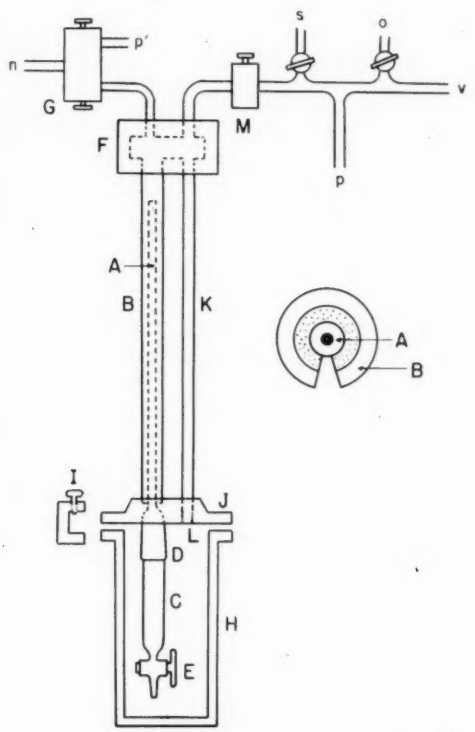

FIG. 1. *Schematic diagram of dilatometric apparatus.* A—glass capillary tube, B—armor tube, C—glass sample tube, D—ground-glass joint, E—stopcock, F—steel ballast chamber, G—three-way valve, H—brass cup, I—C-clamp, J—steel flange, K—brass pipe, L—outlet, M—needle-valve, n—to nitrogen cylinder, o—to atmosphere, p and p'—to mercury manometers, s—to McLeod gage, v—to vacuum pumps.

Apparatus

In the preliminary phase of this investigation an attempt was made to study pore-size distribution of fabrics using the high-pressure apparatus and platinum resistance-wire dilatometer as described by Ritter and Drake [10], with little modification. In this method the operation is carried out in a high-pressure bomb, and the decrease in the height of the mercury in the dilatometer capillary is followed by means of the resistance changes of the platinum resistance-wire mounted inside the dilatometer capillary. The dilatometer is calibrated in terms of cubic centimeters of mercury delivered by the capillary per ohm change in resistance of the platinum wire. The calculated volume changes of the runs are corrected for mercury-in-glass compressibility as determined by a blank run with only mercury in the dilatometer.

The initial pressure (20 p.s.i.a.*) with this apparatus was too high to permit the study of the pertinent pore-size range of the fabrics considered here. Consequently, a new dilatometric apparatus was designed and constructed to cover the range from 5 to 65 p.s.i.a. (20 to 1.6 microns pore radius).

The design of the new dilatometric equipment is shown in Figure 1. A glass capillary tube, *A*, approximately 12 inches long and of uniform bore (2 mm. diameter) is sealed into the armor tube, *B* (brass, ¾ in. inside diameter), with a litharge-and-glycerin cement impregnated with a resin to effect a vacuum-tight and pressure-tight seal. The capillary, which is open at the top, is visible over most of its length through a slot in the armor tube, so that the height of the mercury column in the capillary can be measured with a cathetometer during a pressuring operation. The glass tube, *C*, containing the sample is fitted to the capillary tube through a ground-glass joint, *D*, and the seal is made vacuum-tight with a thermoplastic (glycol phthalic anhydride) resin. The dilatometer is connected to the steel ballast chamber, *F*. Connected to the ballast chamber are a high-vacuum line with an open-end mercury manometer and a three-way valve, *G*, leading to a high-pressure mercury manometer and to a nitrogen tank fitted with a reducing valve. High vacuum is obtained in the vacuum line by means of a mechanical fore-pump in conjunction with a single-stage mercury diffusion

* p.s.i.a. = pounds per square inch absolute.

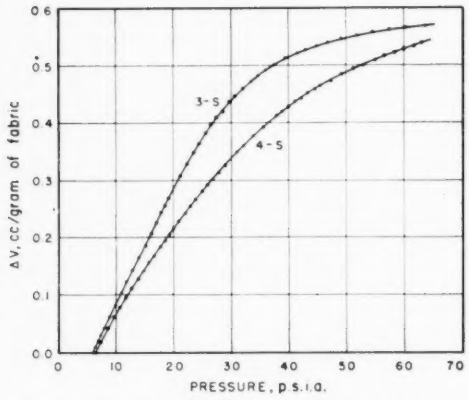

FIG. 2. *Pressuring curves for fabrics 3–S and 4–S.*

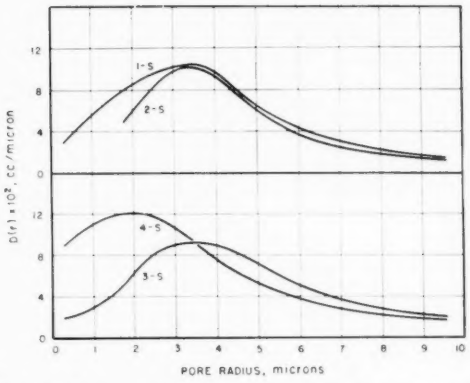

FIG. 3. *Pore-size distribution curves for fabrics 1–S and 2–S (top) and 3–S and 4–S (bottom).*

pump. The mercury manometer on the vacuum side is sufficiently long to obtain measurement of a differential pressure as high as one atmosphere. The manometer on the pressure side is approximately 9 feet high to accommodate pressures as high as 50 p.s.i. above atmospheric pressure. The heavy brass cup, *H*, can be securely fitted with small C-clamps, *I*, to the steel flange, *J*, so that at pressures above atmospheric pressure the sample tube is subjected to pressure both internally through the capillary and externally through the pipe, *K*. At pressures below atmospheric pressure, the cup is not used, and the outlet, *L*, is tightly closed with a threaded brass plug.

The dilatometer was calibrated by determining the volume of mercury delivered from the capillary through the small burette-tipped stopcock, *E*, per millimeter drop in height of the level of the mercury column in the capillary, as measured with a cathetometer. The volume of mercury delivered by the capillary was accurately determined by weighing the mercury and converting to volume with the appropriate density value, and the level of the mercury column in the capillary was read to within ± 0.01 mm. The calibration factor, 0.003185 ± 0.000046 cubic centimeter per millimeter, was found to be quite constant over the entire length of the capillary tube.

Experimental Procedure

In a typical experiment a rectangular piece of the fabric weighing approximately 1 gram is cut out and its weight obtained after drying 1 hour at room temperature under a vacuum of less than 10^{-3} mm. of mercury. The sample, in the form of an open cylinder, is then placed in the sample tube and the tube is sealed into position in ground-glass joint *D* with the thermoplastic resin. The brass plug is inserted at *L* and the dilatometer and sample are thoroughly evacuated. Mercury is then drawn up into the dilatometer by submerging the tip of stopcock, *E*, under the surface of the mercury and slowly opening the stopcock. Care must be exercised to prevent entrapment of bubbles either in the sample or under the mercury, and the level of the mercury must be brought to a starting point sufficiently high in the capillary of the dilatometer. Five minutes are allowed for the penetration of the mercury into the

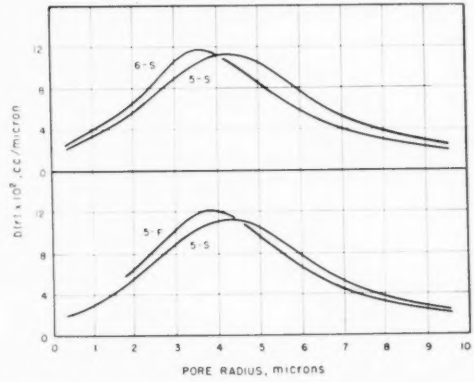

FIG. 4. *Pore-size distribution curves for fabrics 5–S and 6–S (top) and 5–S and 5–F (bottom).*

TABLE I. SUMMARY OF DATA FOR COTTON FABRICS

Fabric designation*	Fabric description	Yarn No. Warp	Yarn No. Filling	Thread count Warp	Thread count Filling	Weight (oz./sq. yd.)	Air permeability†	Pore radius at peak (microns)
1–S	Native	36/2	24/2	127	47	7.99	2.4	3.4
1–F		36/2	24/2	130	47	8.01	1.6	2.6
2–S	Mercerized yarn	34/2	22/2	127.5	48	9.75	1.8	3.35
3–S	Mature	13.8/2	13.8/2	80	32	12.07	2.2	3.6
3–F		13.8/2	13.8/2	80	34	12.32	1.8	3.6
4–S	Immature	13.8/2	13.8/2	80	34	11.62	1.7	2.0
4–F		13.8/2	13.8/2	80	33	11.87	1.1	2.1
5–S	Normal pickage	22.8/2	22.8/2	92.5	38.5	8.30	3.5	4.35
5–F		22.8/2	22.8/2	94	38	8.50	2.5	3.85
6–S	50% more picks than fabric 5	22.8/2	22.8/2	86	59	11.00	2.6	3.6

* S and F designate scoured and finished, respectively.

† Obtained with the Gurley permeometer, conforming to A.S.T.M. "Tentative Method for Air Permeability of Textile Fabrics," D737–46, expressed as cu. ft. per sq. ft. per min.

very largest pores and for the attainment of equilibrium at that initial pressure. The height of the mercury in the dilatometer capillary is then read with the cathetometer.

The initial pressure is obtained from the height of mercury above the mid-point of the sample and is usually about 5 p.s.i.a. After the valve to the vacuum pumps is closed the pressure in the system is increased stepwise by increments of approximately 2.5 cm. of mercury by bleeding air into the vacuum system. After each increase in pressure, a few minutes are allowed for the penetration of the mercury into the fabric pores. Pressure readings from the small manometer are then made simultaneously with the reading of the height of the mercury column in the dilatometer capillary. A definite time schedule for making the settings and readings is desirable for greater consistency of results. When the pressure inside the system has reached atmospheric pressure, the vacuum system is cut out at the needle valve, M, the brass plug is removed from outlet, L, and the heavy cup is quickly fitted into place around the sample tube. Pressuring by increments is then continued from the high-pressure nitrogen tank through a reducing valve and the pressure increase is followed on the large manometer. The maximum pressure obtainable with the apparatus is approximately 65 p.s.i.a.

The decrease in height, ΔH, of the mercury in the capillary is obtained by subtracting each successive cathetometer reading from the initial reading taken before pressuring was begun. These ΔH values are converted to their volume equivalents using the previously determined dilatometer calibration factor. The corrected pressures are obtained by adding the initial head of mercury to the pressures as read from the manometer and subtracting the appropriate ΔH values. In this way, the cumulative volume of mercury in cubic centimeters, ΔV, forced into the pores of the sample for each pressure, p, is determined. Curves 3–S and 4–S in Figure 2 are typical pressuring curves for fabrics in which ΔV in cubic centimeters per gram of sample is plotted against p in p.s.i.a.

The values of the term $\frac{d(\Delta V)}{dp}$ are determined for a number of pressures by measuring the slope of the curve at the various pressures with a device, such as an adjustable quadrangle or a mirror tangent meter. Using these values of the term $\frac{d(\Delta V)}{dp}$ and the values of the pore radius, r, from equation (1), the corresponding values of the distribution function, $D(r)$, are calculated from equation (2). A distribution curve is thus obtained in which $D(r)$ in cubic centimeters per micron per gram of fabric is plotted against r in microns. Several typical distribution curves are shown in Figures 3 and 4. The distribution curves from the lower-pressure apparatus cover an adequate range (down to 1.8 microns) for these fabrics, but the results already obtained with

the high-pressure apparatus are added, thus extending the curves for all the scoured fabrics except 2–S down to 0.2 micron.

Fabrics Studied

Six Oxford-type cotton fabrics were selected for this investigation. These were labeled 1–S to 6–S to indicate that they had been alkali-scoured. Four of these fabrics were also studied after an additional treatment which involved vat dyeing followed by a Zelan finishing treatment. These "finished" samples are designated by the letter "F" after the fabric number. The construction details and other pertinent data for the 10 samples are presented in Table I.

Fabrics 1 and 2 are very similar in all construction features, such as yarn number and thread count. They differ only in that the yarn used in weaving fabric 2 was mercerized. Comparison of fabrics 1–S and 2–S thus affords an opportunity to observe the effects of mercerization in the yarn state on the pore-size distribution.

Similarly, fabrics 3 and 4 are virtually identical in all construction features, as can be seen from Table I. They differ, however, in the fact that fabric 4 was woven from yarn spun from immature fibers, which are in large proportion flat and very thin-walled, while the yarn used in fabric 3 was spun from mature fibers, which are rounder and thicker-walled. These two fabrics were constructed for the purpose of emphasizing the effect of fiber maturity on fabric properties, all other variables having been kept as nearly constant as possible.

Fabrics 5 and 6 were chosen to show the effect of increased pickage. They were woven from the same yarn but fabric 6 has a greater thickness and greater weight per unit area since it has approximately 50 percent more picks per inch.

Results and Discussion

Pressuring curves were obtained in duplicate or triplicate on the 10 selected fabric samples, and corresponding distribution curves were plotted. Since these curves are in most cases very similar in general appearance, only typical curves have been reproduced. The pore-radius values at the peaks of the various distributions are presented in column 9, Table I.

A comparison of the distribution curves for fabrics 1–S and 2–S (Figure 3) seems to indicate that little change has been made in the pore-size distribution by mercerization of the yarn.

The distribution curves for fabrics 3–S and 4–S in Figure 3, on the other hand, show a remarkable contrast. The peak of the curve for fabric 3–S, made from the mature cotton, is in a much higher pore-radius range than that for fabric 4–S, which was made from the immature, thin-walled fibers. For fabric 3–S there is a peak in the distribution curve at approximately 3.6 microns, and for fabric 4–S at about 2 microns. "Fineness" test data showed that the weights per unit length of the constituent fibers in these very similar fabrics are in a ratio of approximately 1.6:1. Since the yarn numbers are identical, this implies that the yarn made from the immature cotton has 1.6 times as many fibers and therefore roughly 1.6 times as many interfiber pore spaces. If the distribution curves follow a similar distribution, the peak for fabric 3–S would be expected to come at a pore-size radius considerably higher than that for fabric 4–S. This is in agreement with the experimental values. Considering this and the fact that these fabrics are practically identical in all structural characteristics, as can be seen from columns 3 through 7 in Table I, little doubt remains that the peaks in these pore-distribution curves are predominantly a measure of interfiber pore-size distribution.

The effect of the 50 percent increase in pickage on the pore-size distribution is shown in the curves for fabrics 5–S and 6–S (Figure 4). Fabric 5–S shows a peak in the distribution at 4.4 microns, and fabric 6–S, with the increased filling count, shows a peak at 3.6 microns. Since in this pore-size range the most significant component of total void space within the fabric is found within the yarn itself—that is, the interfiber space—this shift to a smaller pore-radius range can be logically attributed to the greater compression of the yarns resulting from such a high increase in the filling count.

Since Zelan is essentially an additive finish it might be expected to coat the walls of the pores penetrated, with a resultant decrease in the pore radii. The curves for fabrics 5–S and 5–F (Figure 4) indicate that within the interfiber pore-space range the pore distribution of the Zelan-treated fabric is indeed at a lower pore radius, and from column 9, Table I, it can be seen that fabric 1 shows a similar effect. On the other hand, the radii of the distribution peaks of fabrics 3 and 4 show little or no change as a result of Zelan treatment. It is possible that while Zelan

treatment may tend to cause a shift in the peaks to a smaller pore-size range, the magnitude of the effect is not always great enough to be detected by the present method.

By a comparison of the air-permeability (Gurley permeometer) data with the radii of the peaks of the distributions in Table I it can be seen that for any given fabric, wherever the peak has been shifted by Zelan finishing to a smaller pore size, the air permeability has also been decreased. It cannot, however, be said that wherever a decrease in air permeability is observed a corresponding shift in the peak to a smaller radius has occurred. This is understandable since these peaks represent predominantly interfiber porosity and since other factors contribute to the permeability of a fabric. The interyarn component of porosity may at times be a more significant factor. Thus, as indicated, a shift in the interfiber pore-distribution peak may not be the primary factor in changing the air permeability.

In order to determine whether a relationship exists between the position of the distribution peak and the air permeability for all fabrics studied, the values of columns 8 and 9 of Table I have been plotted in Figure 5. Though the points are few and somewhat scattered, there is a definite indication of a correlation.

It can therefore be concluded that, in general, the distribution curves in the pore-size range here considered can be used as a measure of the relative interfiber pore sizes of different fabrics such as might be due to fiber "fineness" or shape, or yarn compression caused by tightness of weave and perhaps by twist.

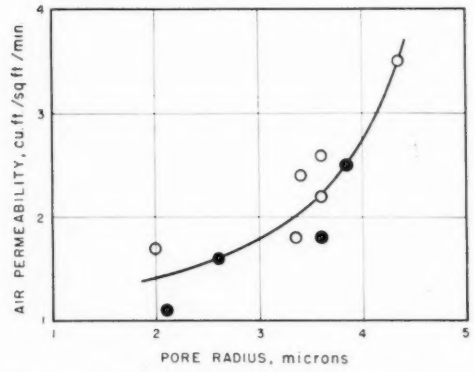

FIG. 5. *Air permeability vs. peak of distribution curve (○, scoured fabrics; ●, finished fabrics).*

TABLE II. COMPARATIVE VOLUMES OF MERCURY FORCED INTO FIBER SAMPLES WITHIN SELECTED PRESSURE RANGES

Pressure range (p.s.i.a.)	Radius range (Å)*	Changes in ΔV (cc./g.)		Ratio Cotton: Rayon
		Cotton	Rayon	
20–10,000	53,000–106	.105	.035	3:1
20–90	53,000–12,000	.067	.028	2½:1
90–382	12,000–2,800	.022	.004	5½:1
382–5,000	2,800–211	.013	.002	6½:1
5,000–10,000	211–106	.004	.002	2:1

* 10,000 angstrom units = 1 micron.

The position of the peak, however, cannot be considered the sole criterion for judging permeability. The height and shape (or sharpness) of the curve together with a consideration of the curve in the larger pore-radius ranges will give more information. The distribution peaks, as presented in this study, represent predominantly interfiber porosity, which may be of less significance in permeability than the interyarn component of the porosity.

Therefore, a new apparatus has been designed which permits the continuation of the distribution curve to 200 microns radius (½ p.s.i.a.). An analysis of volume changes from 2 to 200 microns radius may give a better insight into the relationship between pore distribution and permeability. Such an analysis will be the subject of a future study.

High-Pressure Experiments on Fibers

An attempt was made to determine the pore-size distribution of cotton fibers in the high-pressure apparatus. Pressuring curves were plotted from an initial pressure of 20 p.s.i.a. (in this case, atmospheric pressure plus mercury head over sample) to a maximum pressure of 10,000 p.s.i.a. To determine the effect of the lumens in cotton fibers, similar curves were obtained on viscose rayon filaments. These curves can be considered as consisting essentially of three overlapping sections: (*a*) a rapid rise at relatively low pressures, (*b*) a decrease in slope, gradual for cotton and sharp for rayon, and (*c*) a final almost horizontal section of constant slope. Comparative data read from these curves are given in Table II and show some interesting features.

In the first place, the striking difference in height of the two curves at maximum pressure, at which point the ΔV value for the cotton is approximately three times that for the rayon, can be attributed

FIG. 6. *Photomicrograph of cotton fiber after pressuring to 10,000 p.s.i.a., showing some penetration of mercury into lumens.* (*Magnification 125* ×.)

largely to the fact that the cotton fibers have lumens whereas the rayon has no lumens. From the initial pressure to the reading at the first pressure point (90 p.s.i.a.) the volume change for cotton is approximately 2½ times that for the rayon. In view of the results on the fabric runs, it seems reasonable to assume that this pressure range brings the filling of the interfiber spaces practically to completion, and that the cotton fibers would present more interfiber spaces than the rayon when the shape of the two fibers is compared and the convolutions of the cotton fibers are considered. Within the range from 90 to 382 p.s.i.a., the rayon curve bends sharply toward the pressure axis while the cotton curve is still rising rapidly. Evidently in this range the lumens of the cotton fibers are beginning to show their effect; since the rayon fibers have no lumens, the volume change here would be expected to be small. The final and by far the major portion of the rayon curve is a straight line; although the difference between successive readings is smaller than the accuracy claimed in this experiment, there is an increase in volume filled, as evidenced by a consideration of the total ΔV change within this range. The middle section of the curve for cotton, representing predominantly the filling of the lumen spaces, extends up to a pressure of about 5,000 p.s.i.a. The remaining portion of the curve approximates a straight line the slope of which is about twice that of the straight portion of the rayon curve.

Just what takes place when the cotton fiber is subjected to high pressure under mercury remains, however, a matter of conjecture. The photomicrograph, Figure 6, of a sample of Acala cotton which had been brought to a pressure of 10,000 p.s.i.a. shows definitely that the lumens of some of the fibers have been filled or partially filled with mercury. It is not known whether all of the fibers were completely filled at 10,000 p.s.i.a. (a part of the mercury being trapped on depressuring), or whether filling was only partial (all or most of the mercury that entered the lumens being trapped). In view of the probability of many constrictions along the lumen lengths, it would seem that the latter case is the more likely and that a considerable proportion of the volume change observed on pressuring to 10,000 p.s.i.a. represents a collapsing of the lumen and possibly a compression of the fiber substance. Therefore, any pore-size distribution

curve derived from such a pressuring curve would be subject to considerable doubt. Indeed, those that were so derived showed a "distribution" which was flat from 120 to 5,000 p.s.i.a. and at greater pressures this curve turned sharply upward, and apparently without limit, in the very small pore sizes. The equation for the distribution function (equation (2)) shows that since p/r increases rapidly with increasing pressure, a constancy of the slope term, $\frac{d(\Delta V)}{dp}$, will cause the distribution function $D(r)$ to increase rapidly and without limit. In addition, at higher pressures a very small error in slope determination introduces an increasingly large error in the calculation of $D(r)$ which contributes further to the unreliability of the distribution curve in the very low pore-radius range. Therefore, the nonrigidity of the pore system of the fiber together with the increasing inaccuracy of $D(r)$, due to lack of precision in finding the slope, makes the determination of the distribution curve at such high pressures unreliable, and the pressuring curve itself must be interpreted more as a collapsing effect than as the flow of mercury into the pore system of the fiber.

Summary

The mercury-intrusion method for the study of pore-size distribution developed in the field of petroleum technology was modified to extend the pressure to a lower range and applied to the study of textile fabrics. The pore-size distribution curves obtained for 10 selected fabrics indicate that the method can be used to show significant differences in fabric porosity in the range from about 0.2 micron to 20 microns. The peaks of these curves for all the fabrics studied fall between 2 and 4.5 microns. Analysis of the results shows that these peaks are due predominantly to the interfiber pore-size distribution and that their positions are dependent upon such features as "fineness" or maturity of fiber, and yarn compression.

A comparison of the peaks of the pore distributions with air-permeability data indicates a correlation between the interfiber pore spaces and the air permeability. However, the interyarn porosity may sometimes be a significant factor.

The high-pressure curves for cotton fibers indicate a collapsing of the lumen. This conclusion is supported by the fact that cotton fibers show a volume change three times that of rayon filaments when each material is pressured to 10,000 p.s.i.a. Accordingly, pore-radius distribution curves derived from the pressuring curves obtained at such high pressures on a nonrigid pore system such as that found in cotton fiber are considered unreliable.

Acknowledgment

Acknowledgment is made to other divisions and individual members of this Laboratory for their cooperation in this investigation. The various fabrics were made by the Cotton Processing Division as part of the project on swelling-type, water-resistant fabrics which centered in the Cotton Chemical Finishing Division. Data on the fabric construction and properties in Table I were supplied in great part by the Textile Testing Section. The photomicrograph reproduced in Figure 6 was prepared by the Microscopical Properties Section.

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Degree of Polymerization as Evidence of the Damage to Cotton in Mechanical Processing

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Contribution of the Textile Research Institute and the Department of Chemical Engineering, Princeton University

Abstract

Mechanical processing of cotton causes two types of damage: the first type is physical in nature, resulting from the breaking and bruising of fibers; the second type is chemical in nature, as shown by a decrease in D.P. This change in D.P. is brought about by a mechanical-chemical rupture of molecular bonds and not through a thermal mechanism. A quantitative estimate of the relative damage occurring in each mechanical operation investigated is presented. A loss in D.P of 30 percent was measured as a result of the mechanical operations which converted an Empire seed cotton into yarn.

QUALITATIVE EVIDENCE OF DAMAGE to cotton as a result of mechanical operations has been offered by Clegg [2], who used a Congo red dyeing test to show a general increase in percent of bruised and torn fibers as mechanical processing progressed. However, it has not been shown that chemical degradation accompanies these physical effects. In this paper, chemical actions will be shown to exist and quantitative evidence of the extent of damage in each operation will be presented.

The existence of chemical damage to the cotton as it progresses through the various mechanical processing operations can be easily established if a significant change in D.P., or in molecular weight, of the cotton occurs. Both of these properties can be estimated by viscosity measurements on linear high polymer solutions, according to Staudinger's method [12]. This method was modified by Kramer [4], who introduced the term "intrinsic viscosity" $[\eta]$, which is related to D.P. by an equation of the form

$$[\eta] = K(\text{D.P.})^a, \qquad (1)$$

in which K and a are constants. The values of these constants must be obtained by another technique, as from osmotic pressure or ultracentrifuge measurements. However, even if such calibrations have not been made, the intrinsic viscosity provides a convenient and basically sound index of the molecular weight and may therefore be used to estimate chemical damage involving a change in the length of the molecular chain of the high polymer.

For interpretation of $[\eta]$ in terms of degree of polymerization, the relationship

$$\text{D.P.} = 192\,[\eta] \qquad (2)$$

is a satisfactory estimate for the current work [9]. It has been roughly substantiated by a study of a series of comparative data. However, an exact value is unimportant as long as D.P. and intrinsic viscosity are related in a continuous manner. It is assumed that this will be the case.

If the D.P.-intrinsic viscosity relationship is not linear over the entire range of samples studied, the only modification of the reported results will be a change in percent of total degradation attributed to any specific mechanical process. According to Sadron [10], no great departure from linearity would be expected since the molecular weight range considered in this work is not extensive enough for any possibility of a large effect. It is hoped that a reliable calibration of cupriethylene diamine may appear in the literature in the near future.

The samples used in this study originated from a single bale of Empire cotton obtained from the Georgia Experiment Station of the Department of Agriculture. Cotton from this bale was processed at the School of Textiles, Clemson Agricultural College, Clemson, South Carolina, and samples from the following operations were used: (1) ginning and baling; (2) vertical opening; (3) intermediate

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picking; (4) carding; (5) second drawing; and (6) spinning. A sample of seed cotton from the same lot was also tested.

Experimental Procedure

All samples were dissolved in cupriethylene diamine and the viscosities of these solutions were then measured in capillary viscometers under a series of shear stresses. The details of these operations are described in the following paragraphs.

Solvent

A solution of cupriethylene diamine (0.5*M* in copper) was used as the solvent because of its greater stability to oxygen and light and greater ease of preparation than cuprammonium hydroxide. The method of preparation closely followed that described by Straus and Levy [13] in which the standardization was carried out potentiometrically. The solvent was stored under oxygen-free nitrogen. In Table I, the densities and viscosities of the four batches of solvent prepared to date are presented.

TABLE I. DENSITY AND COEFFICIENT OF VISCOSITY OF FOUR INDEPENDENT PREPARATIONS OF 0.5*M* CUPRIETHYLENE DIAMINE SOLUTION (VALUES DETERMINED AT 25°C)

η	d
1.185	1.047
1.183	1.045
1.186	1.049
1.184	1.047

Samples

From the large samples available for each mechanical operation, small samples used for the viscosity studies were randomly selected. These small samples were placed in a conditioned room for about a week, at which time 3 samples for oven moisture determinations and 6 samples for viscosity measurements were selected and weighed from each of the conditioned process samples. (The latter 6 samples were weighed directly into the test tubes used later in the solution operation.)

Waxes and Pectins

No precautions were taken to remove the waxes and pectins from the cotton samples. Both of these impurities occur in small percentages in cotton and in this study should be nearly constant for all the samples tested. Whistler, Martin, and Harris [14], from a study of the effect of pectic materials on the viscosity of cuprammonium-hydroxide-cellulose solutions, concluded that "the pectic substance does not contribute to the viscosity of cuprammonium hydroxide dispersions of cotton fibers." It should, therefore, be unnecessary to boil the samples in 1 percent NaOH to remove pectic materials, a procedure which might degrade the cellulose and change the D.P. of the cotton samples in an uncontrollable manner. The hot extractions necessary for the removal of waxes would offer similar difficulties. However, since the wax molecules are smaller in size than the cellulose molecules, they make, comparatively, a very small contribution to the total viscosity of the solution. In view of this fact and the small percent by weight of wax in the sample, it is reasonable to believe that any variation in the percentage of waxes and oils from sample to sample would have only a negligible effect, if any, on the cellulose solution viscosities.

Apparatus

The solution (cotton and solvent) was held in a large test tube (7 in. × ⅞ in.). Agitation was accomplished by means of a bent glass stirrer driven by a variable-speed motor. The test tube was also provided with a stopper having an inlet for nitrogen, with leakage around the glass rod providing an outlet. During mixing, the test tube was supported in a constant temperature bath at 25 ± 0.05°C, the same temperature at which the viscosity measurements were made.

Degradation During Solution

It has been stated [14] that degradation of cellulose in cupriethylene diamine is not detectable over the period of time necessary for solution and viscosity determination. However, degradation, as indicated by a decrease in viscosity, was observed in this work, necessitating the use of oxygen-free nitrogen. The oxygen was removed by passing ordinary compressed nitrogen through a medium-porosity Alundum thimble (25 mm. × 70 mm.). The gas, finely dispersed, passed upward through a 15-inch column of alkaline pyrogallol solution in a 1.5-inch-diameter glass tower. The purified nitrogen was tested for oxygen by means of a yellow phosphorus fog trap as described by Zimmerman [15], whereby the cylinder nitrogen passes through the absorption column, the solution test tube, and then the phosphorus fog trap, which served as a check on the elimination of oxygen.

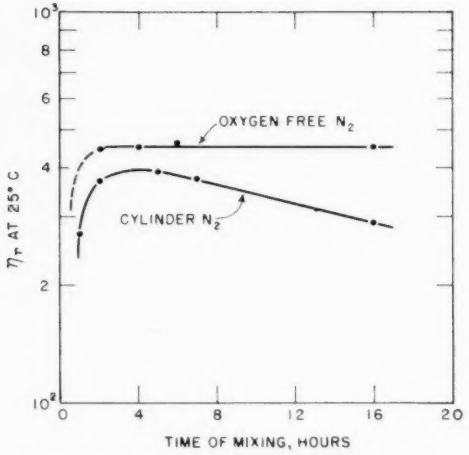

FIG. 1. *Effect of oxygen during cellulose solution.* Lower curve—*Illustration of degradation during solution in oxygen-contaminated* N_2. Upper curve—*Illustration of the lack of degradation during solution in a pure* N_2 *atmosphere.*

For solution of the cellulose, the test tube containing the cotton sample was placed in a constant-temperature bath and the mixer and rubber stopper were set in place. The air in the entire system was then purged with oxygen-free nitrogen, the phosphorus fog trap indicating when the system was completely free of oxygen. Fifteen milliliters of cuprietylene diamine were then added to the test tube and agitation was started. The oxygen-free nitrogen was kept flowing during the entire period (approximately 2 hours) of solution and was checked continuously for oxygen. In this way, the degradation was reduced to such an extent as to be undetectable. An example of the degradation prior to this procedure is illustrated in Figure 1, in which the lower curve was obtained using cylinder nitrogen. This curve may be considered as being made up of two parts: an initial part, with increase in viscosity during solution of the cellulose; a final part, with decrease in viscosity during degradation of the cellulose in solution. The upper curve, when an oxygen-free nitrogen atmosphere was used, does not show the degradation effect. In the upper curve, the viscosity reached a steady value by the end of a 2-hour mixing period. Since this test was run on the highest concentration, a 2-hour mixing period was sufficient to insure complete solution for all samples.

After solution was complete, a 10-ml. sample was transferred to a capillary viscometer, in a constant-temperature bath held at 25 ± 0.03°C. The viscometers used in this work are of the Cannon-Fenske type, for which the calibration constants and dimensions have been determined [1, 6]. The time of flow was measured to the nearest tenth of a second.

Degradation in Viscometers

The time of flow through the viscometer capillary gradually decreased as a result of exposure of the solution to the oxygen in the air. This problem was studied with several solutions of different concentrations by taking readings of time of flow over periods of 6 hours. It was found that a semi-logarithmic plot of time of flow *vs.* time in the viscometer was linear in all cases, indicating a first-order reaction; no exception to this behavior was observed in any subsequent determination. It was also noted that different conditions of shear stress had no effect on the rate of degradation within experimental error. Thus, all measurements, regardless of shear stress, can be extrapolated to zero time

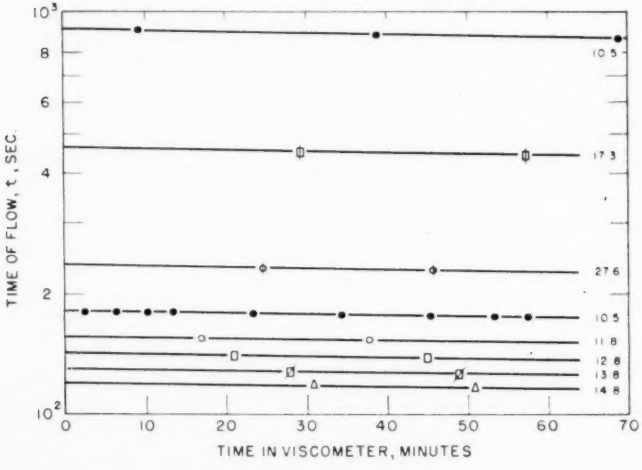

FIG. 2. *Illustration of degradation of cellulose solutions in viscometer; extrapolation technique also indicated.*

(the time at which the solution was transferred from solution tube to viscometer), thereby correcting for the degradation occurring during measurement.

In Figure 2, this method of correcting for degradation is illustrated by two examples. The values at the right of each line are the hydrostatic pressures used. The three upper lines were obtained for a 0.14 g./100 ml. solution, and the lower lines, for a 0.0733 g./100 ml. solution. In both cases, the lines are parallel and extrapolation to zero time can be accomplished easily. The decrease in time of flow is very small but must be taken into consideration if a high degree of precision is to be retained in the method.

Correction for Non-Newtonian Behavior

Since high D.P. cellulose solutions are inherently pseudoplastic, it is necessary to determine the flow rates at several different shear stresses, as discussed in a previous paper [6], and to correct for degradation, as illustrated in Figure 2. Thus, for each sample, at least 9 shear rates were measured—4 at a constant hydrostatic pressure, and 5 at other convenient hydrostatic pressures. In each case, the times at which the solution is transferred to the viscometer and at which each rate is taken are also recorded so that suitable corrections for degradation may be made by extrapolating each rate to zero time along a line parallel to the degradation line established by the points taken at the constant pressure. The viscosity-ratio counterpart was then calculated by means of the following equation:

$$\zeta_r = \left(\frac{4}{Z+3}\right)\left(\frac{\Delta P R_c}{2L}\right)^{Z-1} \frac{t}{t_a}, \qquad (3)$$

the derivation and use of which are explained in the article already noted.

Results

The experimental results, reported in terms of ζ_{sp}/C, are tabulated in Table II. Calculated values of b and $[\eta]$ are also listed in this table. In Figure 3, all of the data for the bale cotton sample and the yarn cotton are plotted. The mean values for the other samples are included for comparison, the individual points having been omitted for the sake of clarity. It is readily apparent that a difference in intrinsic viscosity exists between the bale cotton and the yarn cotton; however, since the other samples are so close to these two, it is essential that all the data be given a statistical treatment, as outlined in the Appendix.

TABLE II.

	C	Z	ζ_{sp}/C	b	$[\eta]$
Cotton from seed	0.0612	1.1983	71.9		
	0.0848	1.3022	135		
	0.0860	1.2620	109		
	0.1083	1.3405	175		
	0.1389	1.4863	298		
	0.2141	1.6330	1125	7.65	26.0
Cotton from bale	0.0254	1.0721	41.3		
	0.1074	1.3190	160		
	0.1382	1.4284	293		
	0.1835	1.5421	570		
	0.2169	1.6116	1014		
	0.2430	1.6852	1695	7.34	26.8
Cotton from vertical opener	0.0487	1.1955	91.3		
	0.0697	1.2253	86.7		
	0.1034	1.3091	147.7		
	0.1358	1.4260	305.9		
	0.1435	1.4275	293.6		
	0.1913	1.4784	448.1	5.64	42.0
Cotton from intermediate picker	0.0644	1.1154	66.1		
	0.0937	1.2643	116.4		
	0.1187	1.3506	189.1		
	0.1450	1.4130	280.6		
	0.1550	1.4171	294.4		
	0.1787	1.4850	432.6	7.07	24.9
Cotton from card	0.0639	1.1427	62.7		
	0.0939	1.2330	194.4		
	0.1190	1.3395	174.0		
	0.1299	1.3724	223.5		
	0.1521	1.4029	251.6		
	0.1928	1.4927	503.8	6.94	24.1
Cotton from second drawing	0.0454	1.1098	50.8		
	0.0975	1.2553	114.8		
	0.1280	1.3472	169.9		
	0.1565	1.4401	321.1		
	0.1960	1.5141	656.0		
	0.2841	1.7282	2447	7.09	23.4
Cotton from yarn	0.0571	1.1346	53.8		
	0.0981	1.2555	108.2		
	0.1180	1.3282	156.0		
	0.1293	1.3491	181.4		
	0.2160	1.5599	827.5		
	0.2931	1.7303	2790	7.35	20.7

Discussion of Results

The results of the statistical analysis show that a significant change occurs in the mean values of ζ_{sp}/C as the cotton proceeds through the cleaning and spinning operations and therefore it may be stated with confidence that the D.P. of the cotton is being decreased by mechanical processing. The intrinsic viscosities, calculated on the basis of the statistical treatment, are tabulated in Table III and illustrated in Figure 4.

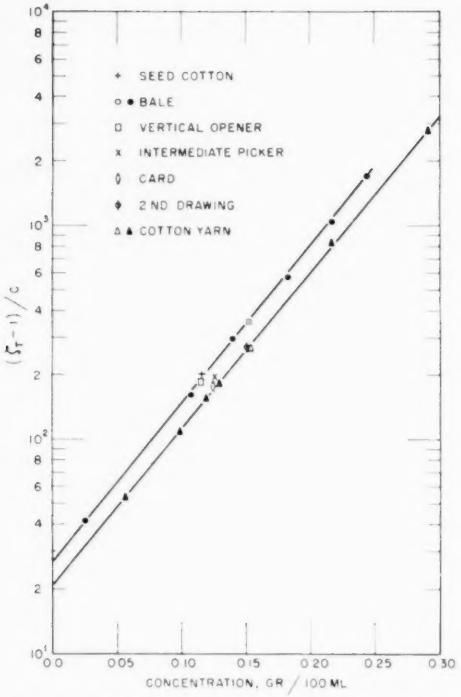

FIG. 3. *Data and method for the determination of the* $[\eta]$ *for the various cotton samples. (Solid symbols represent original data; all other points are for mean values only.)*

A total change of 30 percent in the calculated value of $[\eta]$ occurred from seed cotton to spun yarn. In Figure 5, the percentage of the total estimated damage attributable to each of the operations studied is illustrated. Fifty percent of the damage occurred in the breaker and intermediate picker, 20 percent in the finisher picker and carding operations, and about 18 percent in the ginning operation. Spinning accounted for only 7 percent, and the effect of the vertical opener and drawing operations was negligible.

The type of reaction which causes these changes in D.P. during mechanical processing is not entirely clear. There are at least two possible mechanisms to consider: mechanical and thermal. The energy from the first would be produced by mechanical impact or stress cycling; thermal energy would be supplied in the form of heat, either from an external source or from surface friction; the energy in either case could be utilized in the cleavage of molecular bonds with a consequent decrease in the D.P. Hess and Steurer [3] reported results of work on a similar problem. They compared the thermal degradation of dry cellulose with the mechanical degradation resulting from dry grinding in a "vibrating ball mill." Under their experimental conditions, they found that, while the decrease in $[\eta]$ with time of reaction was very similar in both cases, the temperature coefficient of the mechanical reaction was approximately zero, indicating a zero activation energy (temperature range 0° to 90°C), while that of the thermal reaction resulted in an activation energy of about 19 kg. cal./mol. They also showed that the kinetic energy available from the impact of the balls on the cellulose, if converted directly into molecular vibrational energy, was sufficient to cause the rupture of valence bonds, resulting in a decrease in D.P. That a similar phenomenon is occurring as a result of mechanical processing operations seems entirely logical, particularly as no large temperature rises have ever been observed.

Further evidence supporting the theory of degradation due to mechanical-chemical action was obtained by application of the Congo red test. In this test, the fibers are swollen and dyed and the deepest color shades are localized at previously damaged positions, showing spots or streaks at mechanically damaged locations, or regular spiral patterns when the cuticle has been attacked by heat. Samples from all the processing operations were subjected to this test. Mechanical damage, as observed by Clegg, was readily apparent but not a single indication of the spiral pattern caused by heat was evident. It was concluded, therefore, that the energy necessary for rupture of the cellulose molecules was supplied solely from mechanical action without attendant conversion into heat.

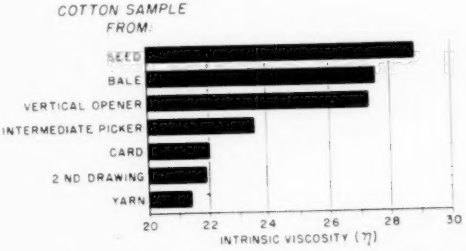

FIG. 4. *Intrinsic viscosity vs. operation.*

TABLE III.

	$(\zeta_{sp}/C)^*$ adjusted mean	$[\eta]^*$ adjusted
Cotton from seed	271	28.8
Cotton from bale	258	27.5
Cotton from vertical opener	256	27.3
Cotton from intermediate picker	221	23.5
Cotton from card	207	22.0
Cotton from second drawing	206	21.9
Cotton from yarn	201	21.3

* Calculated using $b = 7.268$ and $\bar{C} = 0.1339$ in last term of equation (4), as justified by statistical analysis.

Conclusions

Mechanical processing of cotton causes two types of damage to the fibers. The first type is that indicated by the results of the Congo red test, as applied by Clegg [2], which show that the number of bruised and torn fibers increases rapidly as the cotton progresses through the mechanical operations. The second type of damage is that indicated by the decrease in D.P. of the cotton as it is processed, probably resulting from a mechanical-chemical rupture of valence bonds. This degradation is not thermal in nature but is similar to that found by Hess and Steurer in the case of dry grinding of cellulose. Both types of damage undoubtedly have a strong influence on the mechanical properties of the fibers and yarn. The results of the study show that the major damage occurs in the picker operations, indicating that these operations should be the first to be considered in investigating means of decreasing damage resulting from the mechanical preparation of cotton for spinning.

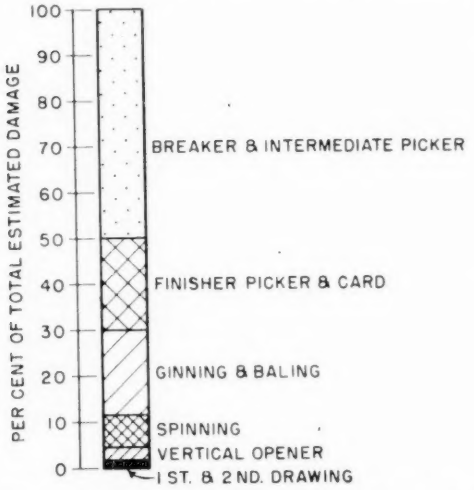

FIG. 5. *Percent of total estimated damage attributable to individual operations.*

Further work is in progress which, it is hoped, will clarify the understanding of the damaging mechanism. Additional samples of processed cotton are also being procured in order that a sounder estimate of the comparative magnitude of the damage attributable to each operation can be made.

Acknowledgment

The authors wish to acknowledge the assistance of the National Cotton Council in obtaining the samples of cotton used in this study, and also to express appreciation to Theodore Lemiszka for the Congo red tests on which part of the conclusions of this paper are based.

Appendix

Analysis of Data

Values of the $[\eta]$ and the slopes of the lines for each of the individual process samples were calculated by the least-squares method using the equation [7, 8]

$$\log \zeta_{sp}/C = \log [\eta] + bC, \qquad (4)$$

where C is assumed to be measured without error. Since the calculation of $[\eta]$ requires an extrapolation to zero concentration of the data represented by this equation, and since the lines for the various samples are not widely separated, visual analysis, with any degree of confidence in the results, is impossible. The slopes do not show any pronounced trend from seed cotton to cotton yarn. From this observation and the fact that the $[\eta]$ is dependent upon the slope, it is obvious that there is too much experimental error to allow a safe extrapolation of the data to zero concentration. Visual inspection indicates that a definite trend exists as one proceeds from ginning to spinning, the value of $[\eta]$ for the vertical opener operation only being out of line. To provide reasonable confidence in the results, the experiments were designed in such a way that results could be analyzed statistically to show whether or not a significant change in D.P. is occurring during the mechanical operations.

Parallelism

If the various lines can be considered to be parallel, it is possible to test the significance of the difference

of the means rather than of the intercepts. This procedure favors the experimenter since the standard deviation of the mean will be less than that of the intercept and differentiation will be apparent even when the actual magnitude of the differences of the intercepts is small. The parallelism test was therefore the first step. This step was made using the Snedecor ratio [11]

$$F = \frac{\sum_{i=1}^{m} w_i(b_i - \bar{b})^2}{m-1} \Big/ \frac{\sum_{i=1}^{m}\sum_{\alpha=1}^{n} d_{y\cdot x}{}^2}{m(n-2)}, \qquad (5)$$

where

$$\frac{\sum_{i=1}^{m} w_i(b_i - \bar{b})^2}{m-1}$$

is the variance of the slopes of the lines, and

$$\frac{\sum_{i=1}^{m}\sum_{\alpha=1}^{n} d_{y\cdot x}{}^2}{m(n-2)}$$

is the variance attributable to experimental error. The data for the samples from the vertical opener were omitted from this analysis, as the value of $\Sigma d_{y\cdot x}{}^2$ was so much greater than that for the remaining 6 samples that a lack of homogeneity of the variance, which is attributable to some experimental error not common to the other sample series, is obvious. The Snedecor ratio in this analysis was less than unity, indicating that the variance of the slopes was of the same order of magnitude as, and attributable only to, experimental error. Concluding therefore that the lines were parallel, the average of all the regression slopes was used in testing the significance of the difference of the means by an analysis of covariance [11]. In this case, $F = 6.36$ ($F_{.01} = 3.38$) was well above the 1-percent level, indicating that the means of the values of ζ_{sp}/C are significantly different. It may be concluded that there is a significant change occurring in the $[\eta]$ of the various process samples and that the adjusted mean of ζ_{sp}/C is the best estimate available to show these changes. The summary of these results (the adjusted mean, ζ_{sp}/C, at C for each operation) is given in Table III.

[Further tests are in progress on samples of Stoneville 2B cotton obtained through the cooperation of C. M. Conrad and R. J. Cheatham of the Southern Regional Research Laboratory. Preliminary results of tests on cotton from the bale and in the yarn form indicate a damage equivalent to that which was determined on the Empire cotton. They also show that the values of $[\eta]$ for these two samples are in the same range as those measured on equivalent samples of the Empire cotton.—*Editor*]

Nomenclature

a—constant
b_i—regression coefficient of the ith line
$\bar{b}$—mean regression coefficient
m—number of lines
n—number of points per line
o—subscript, refers to solvent
C—concentration, g. 100 ml.
D.P.—degree of polymerization
K—constant
L—length of capillary, cm.
ΔP—hydrostatic pressure, g. cm. sec.
R_c—radius of capillary, cm.
Z—slope, $d(\log 1/t)/d(\log \Delta P)$
ζ—viscosity counterpart
ζ_r—viscosity-ratio counterpart, ζ/η_o
ζ_{sp}—specific-viscosity counterpart, $\zeta_r - 1$
η—coefficient of viscosity
η_{sp}—specific viscosity, $\frac{\eta}{\eta_o} - 1$
$[\eta]$—intrinsic viscosity, $\lim_{C\to 0}(\eta_{sp}/C)$, Newtonian; $\lim_{C\to 0}(\zeta_{sp}/C)$, pseudoplastic

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Urea as a Solvent Aid for Cellulose Textile Sizes

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Abstract

Urea was evaluated as a solvent aid for alkali-soluble ethylene oxide ethers of cellulose which are suitable as textile sizes. It was not found to be an economical aid for this purpose, although it apparently reduced solution viscosity. The ratios of caustic to water and cellulose ether to water were shown to be the main factors controlling solution viscosity. Based upon the fact that urea has a very high partial and apparent molal volume in aqueous solutions, it is suggested that urea acts as an inert diluent when incorporated into alkaline solutions of the ethylene oxide ethers. Further, it was shown that urea could bring about either increases or decreases in the viscosity of these ether solutions, depending upon whether urea is added to or replaces water in any given system.

THIS INVESTIGATION was undertaken to evaluate urea as a solvent aid for the preparation of aqueous alkaline solutions of ethylene oxide ethers of cellulose and to find a possible explanation for the apparent lowering of viscosity brought about by the urea.

Recent publications have aroused interest in urea either as a solvent aid or as an additional component for preparing aqueous alkaline solutions of cellulose or cellulose derivatives. Carboxymethyl and ethylene oxide ethers are among the derivatives which may be employed as textile sizes. Mantell [6] pointed out that the incorporation of urea into aqueous sodium zincate and stannate solvents made it possible to prepare cellulose solutions which at room temperature possessed substantially lower viscosities than similar solutions which contained no urea. Seymour [8] presented data to show how the addition of urea to aqueous solutions of the above cellulose ethers caused a decrease in viscosity. In this same paper, it was noted that urea had no influence either on the viscosity of cellulose in ammonical copper hydroxide or on polyvinyl alcohol in water. No attempt was made to reconcile the peculiar action of urea in these connections.

The behavior of urea toward cellulose is unique in many respects—for example, in its swelling action on wood and cellulosic substances [2, 4]. Swelling by lyotropic substances, including urea, in aqueous alkali is apparently not caused by specific compound formation but must depend upon surface phenomena [4]. Urea causes a drop in surface tension of water [5, 9] and behaves in aqueous solution in a manner approaching that of the perfect solute, in so far as its partial and apparent molal volumes are concerned [3].

A four-component system such as urea-caustic-water-cellulose ether is very difficult to interpret, for a change in any one component necessarily displaces the relationships existing between all components. In interpreting viscosity changes in aqueous alkaline solutions of cellulose or cellulose ethers, two of the most important considerations are concentration of cellulosic substance and concentration of alkali.[1] These are widely acknowledged facts and will be considered principally in this discussion, although admittedly there may be other factors involved.

Experimental Procedure

Two types of alkali-soluble ethylene oxide ethers (based on average degree of substitution) were employed in this investigation. Type I had an average degree of substitution of 0.38 group per glucose unit [7] and a specific viscosity of 1.223 * [1]. Type II had an average degree of substitution of 0.19 group per glucose unit and a specific viscosity of 1.024. A number of solutions were prepared

* Determined on a 0.5% ether solution in standard cuprammonium solvent. Sample weights were corrected for average degree of substitution. For procedure see [1].

TABLE I. COMPOSITION AND VISCOSITY OF 6% SOLUTIONS OF ETHYLENE OXIDE ETHERS OF CELLULOSE

Solvent composition as made up (g./100 cc.)		Effective concentrations (g./100 cc. H_2O)		Solution viscosity, sec. (25°C)	
NaOH (1)	Urea (2)	NaOH (3)	Cellulose ether (4)	Before cooling (5)	After cooling (6)
Type I ether					
3	0	3.00	6.00	19.7	13.1
3	10	3.24	6.48	—	11.4
3	17	3.44	6.88	9.6	8.8
4	0	4.00	6.00	9.6	7.5
4	10	4.33	6.48	—	8.0
4	16	4.55	6.82	7.1	6.4
5	0	5.00	6.00	6.6	5.6
5	6	5.24	6.28	—	7.4
5	10	5.41	6.48	—	7.5
5	15	5.64	6.76	5.7	6.1
5	20	5.89	6.81	—	6.7
6	0	6.00	6.00	5.7	4.7
6	10	6.48	6.48	—	6.4
6	14	6.72	6.72	6.3	5.5
Type II ether					
4	0	4.00	6.00	—	—
4	10	4.33	6.48	—	9.0
4	16	4.55	6.82	38.7	11.6
5	0	5.00	6.00	45.6	12.0
5	10	5.41	6.48	—	5.7
5	15	5.64	6.76	9.0	5.6
6	0	6.00	6.00	13.6	5.9
6	5	6.23	6.15	—	4.9
6	10	6.48	6.48	—	5.1
6	15	6.76	6.76	—	5.0
7	0	7.00	6.00	7.0	5.0
7	13	7.76	6.65	5.9	5.3
8	0	8.00	6.00	—	4.6

containing 6 g. (dry weight) of these ethers where the alkali and urea contents of the solvent were varied. Solutions were made up in glass-stoppered flasks at 22°C and were rotated for 14 hours. Entrapped air and gas bubbles were removed *in vacuo*, then viscosities were measured at 25°C. Viscosity values in Table I were determined employing a $\frac{1}{8}$-inch-diameter steel ball in standard viscosity tubes. These tubes were 30 cm. long and 1.9 cm. in diameter.

The experimental error was ± 0.15 sec. These same solutions were chilled at − 15°C in a brine bath for 2 hours, then another viscosity sample was removed and run.

The solutions listed in Table II were made up to demonstrate how viscosity in this system may change with the manner of solution preparation. Each solution (1–4) was initially prepared with the same amount of cracked ice, the same stirring speed, and the same over-all solution time of 2 hours. Solu-

TABLE II. VISCOSITY DEPENDENCY ON MODE OF SOLUTION PREPARATION

Type II ether* Solution No.	System composition (g./100 cc. solution) Ether	NaOH	Urea	Solution viscosity (C.P., 30°C)
1	6	6	10	1,168
2	6	6	0	928
2+10 g. urea	5.58	5.58	9.30	776
1+7.5 cc. H_2O	5.58	5.58	9.30	776
3	6	6	10	416
4	6	6	0	179

* Solutions 3 and 4 were made from an ether having specific viscosity 1.024.

TABLE III. VISCOSITY LOSS ON AGEING AQUEOUS ALKALI-UREA-CELLULOSE ETHER SYSTEM AT 30°C

Ageing time (hrs.)	Solution viscosity (C.P.) System composition (g./100 cc. solution) 6 ether 6 NaOH 10 urea	6 ether 6 NaOH 0 urea
0.0	416	179
15.5	366	163
21.0	358	160
40.0	346	146
114.0	318	148
162.0	307	134
Final % loss in solution viscosity	26.2%	25.1%

tions 3 and 4 were further aged in closed systems at 30°C to determine whether or not urea-containing solutions differed in ageing characteristics from the ordinary alkaline solutions (Table III). The viscosity values in Tables II and III were determined with a Brookfield Viscosimeter of the Stormer type.

Various amounts of urea were incorporated into standard cuprammonium solvent [1], which was then used to dissolve a regenerated cellulose (average basic D.P. of 496). The solutions were prepared in the standard manner and the urea content was expressed as weight per unit volume of solvent (Table IV).

Discussion of Results

The two types of cellulose ethers employed had different solubility and solution characteristics. On the one hand, type I, being of higher substitution, was more easily soluble and reached a minimum viscosity in an alkaline solvent of about 8% concentration. Viscosities in this case, although changed by, were not critically dependent upon changes in

alkali concentration of from 5% to 10%. Workable solutions were easily made in 3% caustic. On the other hand, type II ether, of lower substitution, reached a minimum viscosity in about 8% caustic, but changes in concentration of alkali from 5% to 10% were more critical; and over 4% caustic was required to give solutions at room temperature. Figures 1 and 2 (Table I) show these results. They are cross plots of the series of curves obtained by plotting urea content (column 2) against final viscosity (column 6).

One of the main points stressed by previous workers [6, 8] concerning urea as a solvent aid was that the use of urea gave solutions of substantially lower viscosities. Figures 1 and 2 demonstrate that this observation is true in a sense. These curves represent solutions all of which contained the same concentration of cellulose ether per unit volume of solvent, but each solution actually had different alkali-to-water and cellulose-ether-to-water ratios. This was necessarily so when urea was employed to replace water in the system because of its high partial molal volume. The values in columns 3 and 4 (Table I), the effective concentrations of caustic and cellulose ether with respect to water, were calculated on the basis that the partial molal volume of urea at 25°C was very close to 45.19 cc. per mole [3]. This meant that for every gram of urea placed in the system, approximately 0.75 cc. of water was replaced. The solutions, while having the compositions indicated in columns 1 and 2, had very closely the compositions shown in columns 3 and 4 with respect to water. The very small volume change occurring when caustic was added to the system was neglected when compared to the large change brought about by the addition of urea.

TABLE IV. VISCOSITIES OF CUPRAMMONIUM SOLUTIONS OF CELLULOSE CONTAINING UREA AT 20°C

Urea (%)	Specific viscosity	
	Cellulose (0%)	Cellulose (1%)
0	0.0000	2.962
5	0.0144	3.070
10	0.0204	3.139
15	0.0375	3.280
20	0.0541	—

Considering only apparent solution compositions and viscosities (Figures 1 and 2), it was evident that urea decreased the viscosity of type I ether when the alkali concentration was below 4 g. per 100 cc. of solvent. In the case of type II ether, a less soluble type, the same trend was observed below an alkali concentration of 6 g. per 100 cc. of solvent. At alkali concentrations above these values urea apparently caused increases in the observed viscosities. This was the over-all influence of both the alkali-to-water and the cellulose-ether-to-water ratios being simultaneously increased. The increase in the

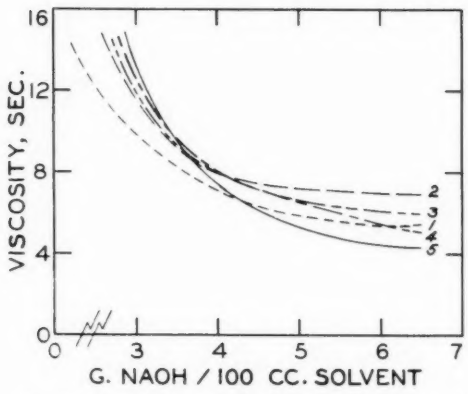

FIG. 1. *Viscosities of 6% cellulose ether (type I) solutions containing urea. Curve 1—15 g. urea per 100 cc. solvent. Curve 2—10 g. urea per 100 cc. solvent. Curve 3—7.5 g. urea per 100 cc. solvent. Curve 4—2.5 g. urea per 100 cc. solvent. Curve 5—No urea.*

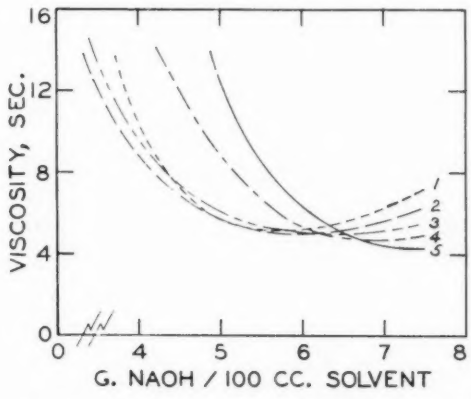

FIG. 2. *Viscosities of 6% cellulose ether (type II) solutions containing urea.. Curve 1—15 g. urea per 100 cc. solvent. Curve 2—10 g. urea per 100 cc. solvent. Curve 3—7.5 g. urea per 100 cc. solvent. Curve 4—2.5 g. urea per 100 cc. solvent. Curve 5—No urea.*

alkali-to-water ratio decreases viscosity to a greater extent than the increase in the ether-to-water ratio increases it. After the maximum effective alkali concentration was reached, any further increase in the alkali-to-water ratio would also act to increase viscosity. As a result, the viscosity-caustic concentration curves were effectively displaced with increasing urea contents toward the intersection of the x and y ordinates along the x-axis.

That urea really acted as an inert diluent which was highly compatible with aqueous alkaline solutions of the cellulose ethers was further substantiated by data in Table II. If, on the one hand, urea was incorporated into a solution, replacing water, the viscosity was increased. If, on the other hand, it was added to a solution, then the viscosity decreased, because of a dilution effect which was very similar to that obtained when water was added. Assuming this reasoning to be correct, then the same type of results should be observed in cuprammonium solutions of cellulose when the cuprammonium solvent is replaced by urea. Table IV shows this to be true. Solution viscosities and specific viscosities of cuprammonium solvents and cellulose systems containing urea increased linearly with urea content. Observed changes were small in this case and might not have been noted if a less sensitive measurement of viscosity had been used. The relatively slight influence can probably be attributed to the fact that cuprammonium has a greater solvent power for this regenerated cellulose than aqueous alkali has for these particular ethylene oxide ethers.

The presence of urea in alkaline solutions of these ethers did not result in a reduced rate or degree of solution ageing (Table III). By measuring viscosities prior to the chilling step (Table I, column 5), it was found that chilling the alkaline solutions brought about an effect similar to incorporating urea into, or adding urea directly to, the solvents. It further was observed that, depending upon the original ether type, adding 5 to 10 g. of urea per 100 cc. of solvent was only as effective as increasing the caustic concentration by about 0.5 g. per 100 cc. of solvent.

Each solution represented in Table I was diluted to twice its original volume with water, and urea was not found to contribute to the dilution stability of the type I ether. It did extend the gelation time slightly in the case of type II ether. These last observations conform with the view that incorporating urea into the aqueous alkaline solvents either effectively increases the actual caustic-to-water ratio, or causes a dilution, both of which factors are important in changing the solution viscosities.

Summary

Urea may or may not reduce the observed solution viscosities of the ethylene oxide ethers of cellulose dissolved in aqueous alkali, depending upon how the solutions are made up. It does not appear to be an economical aid in reducing the solution viscosities of these ethers for use as textile sizes. A borderline case which might need chilling to obtain solution requires ten to fifteen times as much urea as additional sodium hydroxide to attain solutions at room temperature.

Urea appeared to act as an inert, highly compatible diluent in causing apparent decreases in viscosity because of its high partial molal volume in aqueous solutions. The ratios of sodium hydroxide to water and cellulose ether to water appear to be the true governing factors in changing viscosity.

Acknowledgment

The author wishes to thank Mr. O. A. Battista for obtaining all data based on cuprammonium viscosities and the members of the Analytical Section of the Chemical Research Department for their cooperation.

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INDUSTRIAL SECTION

The Spectrophotometer as an Aid to Dyeing

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A contribution from the Research Laboratory of Sidney Blumenthal & Co., Inc.

Abstract

Dyeing as it is known today in the textile industry is a technical process which has recently graduated from the stage of being an art to becoming a science. The primary thing responsible for this change is the control of the variables in the process. The spectrophotometer is a physical tool which is eminently suited to measure the most important variable of all, the shade and strength of the dyestuffs themselves, whether they be in solution or on the fiber. The general principle of operation of several of these instruments is explained. In practical applications of color measurement, some of the techniques employed to obtain and translate spectrophotometric data into useful information are discussed. Examples of these are standardization of both water-soluble and certain insoluble dyes; measurement of production dye-mixture solutions and print pastes in order to control the color before their use on fabric; qualitative and quantitative estimation of dyes on the fiber; and study of the mechanism of the dyeing process itself.

THE LANDMARKS of technological progress in the textile industry are the successful applications of developments garnered for the most part from other less complex industries to solve problems peculiar to textiles alone. Not infrequently are such evolutions heralded as the "cure-all" for the industry's ills, past, present and future; such was the ignominious role that the spectophotometer played to the textile dyer some years ago. Many foolhardy claims were made of the ability of the spectrophotometer to match shades, eliminate all but the most rudimentary labor in the dyehouse, and all that the dyer would have to do would be to own such an instrument and his troubles would be over. If anyone knows a little about the dyeing of textiles he can readily appreciate that such a utopian situation does not evolve simply from the purchase of one or more instruments of any sort. And it is further apparent that a color-measuring instrument such as the spectrophotometer can be a useful and powerful tool to aid the dyer provided that the necessary amount of development work goes into the application of the instrument to any given problem. The "spectro" is merely an optical instrument which measures color in purely physical (science) terms; the interpretation of the physical data thus obtained into usable knowledge is the crux of the problem.

In order to understand the application of the spectrophotometer, it is necessary to examine briefly a few of the more important commercially available instruments. Most "spectros" have a few features in common: White light from an incandescent bulb is broken up into the spectrum, and discrete portions of this spectrum are examined at any one time. The reflection or transmission of any given sample is compared to that of a standard at a specified point in the spectrum by electronic and/or electromechanical means; a series of points so determined when connected will give a curve which is the physical representation of the color of the measured specimen.

First let us consider the G. E. Recording Spectrophotometer [4, 5, 7, 8], which is shown in general view in Figure 1. It is easier to understand the

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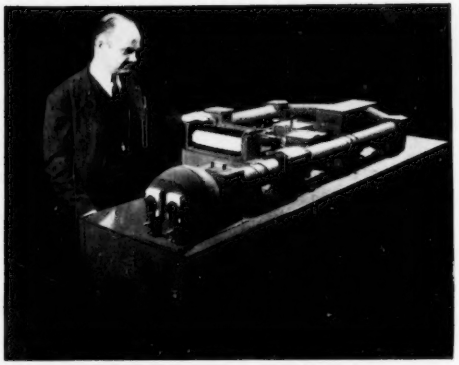

FIG. 1. *G. E. Recording Spectrophotometer. General view of instrument in operation. (Courtesy General Electric Company.)*

principles of operation of the instrument from examination of Figure 2, a schematic diagram. The monochromator, the part of the instrument which breaks up the light into the spectrum, is linked directly to the chart on the recorder drum, driving it is such a manner that its horizontal position is directly proportional to the selected portion or wave length of the spectrum. The photometer is the measuring unit which compares the reflection or transmission of the sample to the standard; the photometer is linked to the pen drive which moves the pen vertically across the sheet. The resultant curve, when drawn through the complete spectrum, is the physicist's "color curve," with reflection or transmission as the abscissa and wave length as the ordinate.

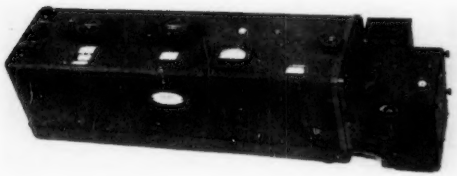

FIG. 3. *Model DU Spectrophotometer. General view with 1-cm. cell compartment. (Courtesy National Technical Laboratories.)*

An instrument which is presently non-recording but is widely used for transmission measurements in the ultraviolet region as well as in the visible and near infrared is the Beckman Model D U "Spectro" [1, 3] shown in general view in Figure 3. The schematic diagram (Figure 4) of the monochromator shows that it is quite different from the G. E., but, being of quartz, it permits measurements down to 215 millimicrons in the ultraviolet. The standard and the sample must be manually interchanged for comparison on the electrical scale of the instrument and a complete spectral curve can be drawn from a series of point readings. Reflection (Figure 5) and fluorescence measurements are made with appropriate attachments. Another accessory for this instrument which is of particular interest to chemists is the Beckman Flame Photometer. A recorder attachment is planned for sale in the near future.

The newest development in "spectros" [9] is the Beckman Model B Spectrophotometer (Figure 6),

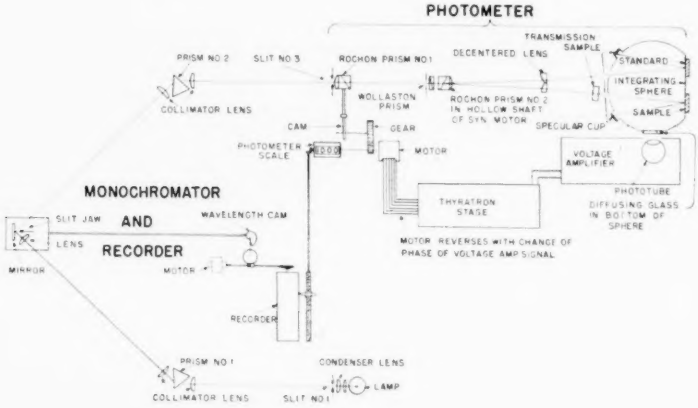

FIG. 2. *G. E. Recording Photoelectric Spectrophotometer. Schematic diagram with parts named. (Courtesy General Electric Company.)*

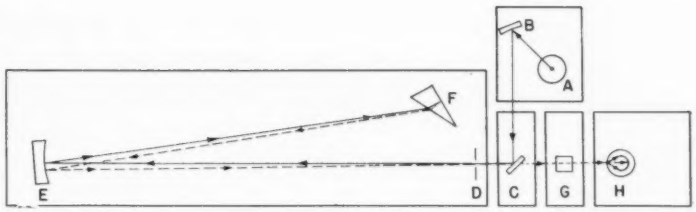

FIG. 4. *Optical system of Model DU Spectrophotometer. A—Light source. B—Concave focusing mirror. C—Plane mirror. D—Slits. E—Collimating mirror. F—30° Littrow mounted quartz prism. G—Absorption cell (for solutions). H—Photocell. (Courtesy National Technical Laboratories.)*

which is mainly a simplified version of the Model D U, which has borosilicate glass rather than quartz optics. The optical system is much the same as that of the D U, except for over-all size (Figure 7); the Model B is A. C. line-operated rather than dependent upon batteries for its voltage supply. This new instrument offers considerable promise for applications requiring a non-recording instrument with a wave-length range which includes the near ultraviolet, visible, and near infrared spectra. There will be a reflection measurement attachment available for the Model B "spectro."

Another fairly new instrument is the Cary Recording Quartz Spectrophotometer shown in Figure 8. Although this is a custom-built instrument, there are a number of them in use throughout the U.S.A. Optically, the "spectro's" monochromator looks something like the Beckman Model D U's except that the Cary has a double manochromator which gives much better resolution (see Figure 9). The beam is split, after passing through both prisms, into two equal parts, and the radiant energy is received on a pair of matched multiplier phototubes; the output of the phototubes is compared electronically to give the photometric scale for measurement of reflection and transmission. Recordings of spectral curves are made with a high-speed Brown recorder which is linked to the automatic photometering scale. Samples in the instrument are measured relative to standards, as in the case of the G. E. instrument. With quartz optics, the ultraviolet range is as readily available as the visual range.

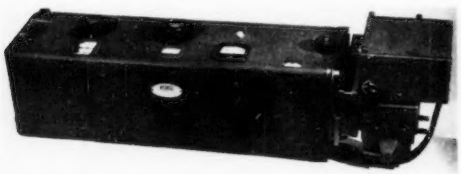

FIG. 5. *Model DU Spectrophotometer with reflection accessories. (Courtesy National Technical Laboratories.)*

FIG. 6. *Model B Spectrophotometer. General view. (Courtesy National Technical Laboratories.)*

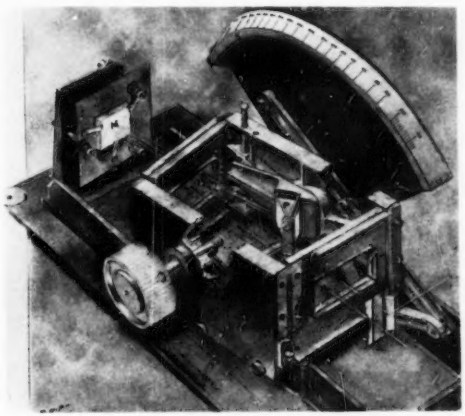

FIG. 7. *Wavelength drive and prism mount of the Model B Spectrophotometer. S—Exit and entrance slits. M—Collimating mirror. P—Féry prism. (Courtesy National Technical Laboratories.)*

TABLE I

Instrument	Recording	Reflection attachment	Range (millimicrons)	Approx. effective band width	Cost
G. E. Recording Spectrophotometer (General Electric Co.)	Yes	Standard part of instrument	400–1,000	10 mμ (30 mμ) (700–1,000)	High
Beckman Model DU Spectrophotometer (National Technical Labs.)	No. Contemplated for near future	Available	215–1,000	2 mμ (10 mμ) (700–1,000)	Medium
Beckman Model B Spectrophotometer (National Technical Labs.)	No	Will be available	325–1,000	5 mμ	Low
Cary Recording Quartz Spectrophotometer (Applied Physics Corp.)	Yes	Available	215–800	0.1–0.4 mμ	High

In Table I an attempt has been made to give a résumé of the features of the several instruments described above. The whole fields of infrared, x-ray diffraction, mass and emission spectra have purposely not been mentioned, since these are of primary interest only to the chemist and the physicist. The dyer and the textile chemist are mainly interested in the visual spectrum, and ultraviolet spectra are mentioned only because certain instruments incorporate them with the visible.

The application of the "spectro" to dyeing comes about in many different ways [10, 13]. The objective which the dyer strives for is frequently termed "formula dyeing"; if this ideal were achieved, once a formula was established all that the dyer would need to do would be to put a batch of cloth in a kettle with a given amount of dye and out it would come, exactly the same shade every time. The "spectro" obviously does not necessarily make that possible, but it can go a long way towards *helping* to achieve that end. It is up to some worker in a textile mill to recognize the problems involved; the "spectro" may offer the solution to those problems but cannot effect a remedy.

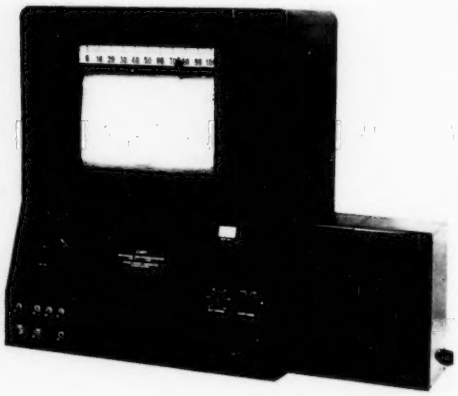

FIG. 8. *Cary Recording Quartz Spectrophotometer. General view showing a recording of the ultraviolet absorption spectrum of benzene. (Courtesy Applied Physics Corp.)*

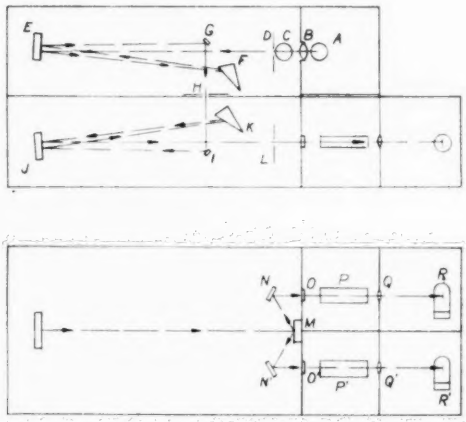

FIG. 9. *Optical system of the Cary Recording Quartz Spectrophotometer. A—Lamp. B—Lens. C—Cylindrical shutter. D—Entrance slit. E and J—Collimating mirrors. F and K—Quartz prisms. G and I—Mirrors. H—Intermediate slit. L—Exit slit. M—Beam splitter. N and N'—Collimating mirrors. O and O'—Stops. P and P'—Absorption cells. Q and Q'—Focusing lens. R and R'—Multiplier phototubes.*

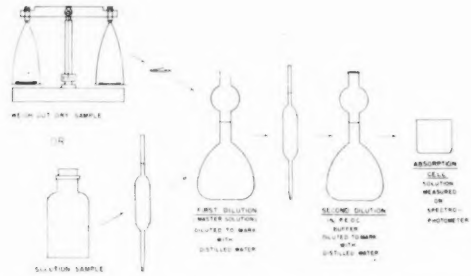

FIG. 10. *Basic procedure for preparing spectrophotometer solutions.*

In relating the applications of the "spectro" in one textile plant, rather than attempt to recount all of the numerous methods which are used in connection with color-measurement work we will describe a few selected procedures which are specialized and might be of interest. It is generally accepted that the water-soluble dyes which are purchased by a textile mill can be tested more accurately and more cheaply by spectrophotometric means. This is done in a routine manner for all dyestuffs by most mills that own a spectrophotometer. We use a basic procedure, shown in Figure 10, for preparing solutions of water-soluble colorants. As an evolution from the dye-testing techniques of soluble dyes, we have developed special methods for handling certain of the insoluble dyes, recognizing their chemical characteristics. For example, the azoics (ice colors) can be both qualitatively and quantitatively measured. The concentration of the one component, the Naphthol AS (2-hydroxy-3-naphthoic acid anilide) homologue, is determined colorimetrically as its derivative formed by coupling with diazotized sulfanilic acid; the resultant dye is soluble in 50% alcohol [2]. For determination of the strength of the other "half-dye," the fast color salt (*e.g.*, Fast Red Salt GL—3-nitro-4-toluidine diazonium chloride), it is coupled to a fixed amount of a water-soluble naphthol-sulfonic acid such as R Salt (2-naphthol-3:6-disulfonic acid sodium salt). The water solution of the dye formed by this coupling is measured on the "spectro," permitting quantitative estimation of fast color salts.

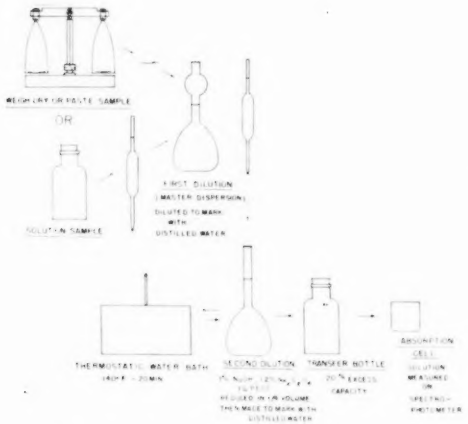

FIG. 11. *Special procedure for vat dyes.*

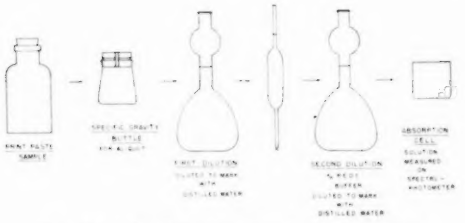

FIG. 12. *Special procedure for print pastes.*

The procedure for strength evaluation of the components of azoic dyes is merely an adaptation of the basic method used for soluble dyes shown in Figure 10. The special chemical agents which are used to produce a dye from the components are introduced into either the first or the second dilution, depending upon convenience. The well-known class of colorants known as vat dyes owe some of their superior fastness properties to their water-insolubility. In normal application of vat dyes to textiles, the dye is chemically reduced and dissolved in alkaline solution so that it will dye the fiber; it is subsequently oxidized back to its original state. The solution of the reduced vat dye is what we measure. The color of this solution, although different, is correlated with the color of the oxidized dye. Several features of the method are shown in Figure 11. The objectives of the procedure are: (1) to attain reproducible conditions of dye reduction; (2) to prevent oxidation of the colorant; and (3) to limit the oxidation of the reductant, sodium dithionite.

Thus far we have discussed the case of the single dye (or half-dye), which is a part of the usual program of testing raw materials upon delivery to the plant. However, more emphasis can be placed upon actual production controls when a tank of dye liquor

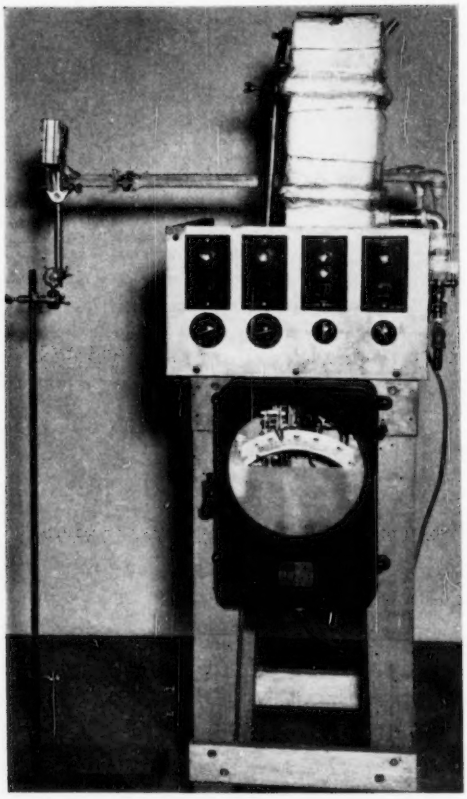

FIG. 13. *Spectrophotometer dyeing machine. General view, with cell attached.*

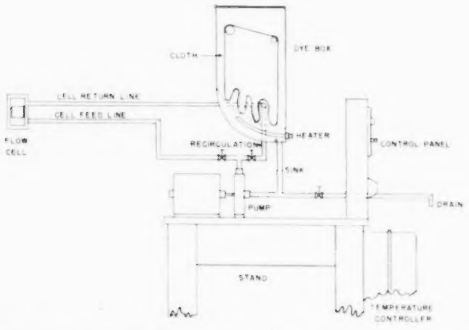

FIG. 14. *Spectrophotometer dyeing machine. Diagrammatic cut-away view.*

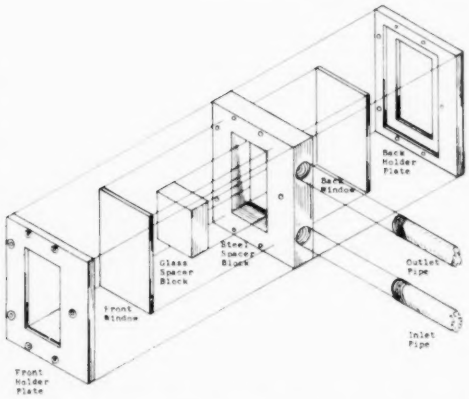

FIG. 15. *Spectrophotometer dyeing-machine absorption cell. Exploded isometric view.*

is sampled and examined before use. The usual shades common to pile fabric textiles are dyed with combinations of from two to eight dyes, depending upon fiber composition and the color. The procedure in testing dye liquors is to compare successive batches with an original one which has been established as acceptable. Sometimes a first approximation of the strength of the individual components in a dye mixture is sufficiently good for processing purposes. This means that we merely take the transmittance at the absorption maximum of a given dye and compare it at the same wave length to the transmittance of a similar mixture established previously as standard. This calculation is necessarily in error because of the absorption of the other components in the mixture at that given wave length. When more accurate data are required, the computation is carried through completely, using the reciprocal matrix method. This method, as suggested by Saunderson and Grossman of the Dow Chemical Company [12] for use with a computer, has been found to give excellent results in our work, where the same shade is dyed repetitively over long periods of time. The coefficients, or "alpha's," of the reciprocal matrix are preliminarily solved on a Monroe calculator. Once the "alpha's" are established, we are able to complete the average computation in little more time than it takes to calculate the first approximation.

A slightly different technique is used in connection with the problem of color control of textile printing, since a print paste is just what the name suggests—a thick, viscous solution of dye which can be trans-

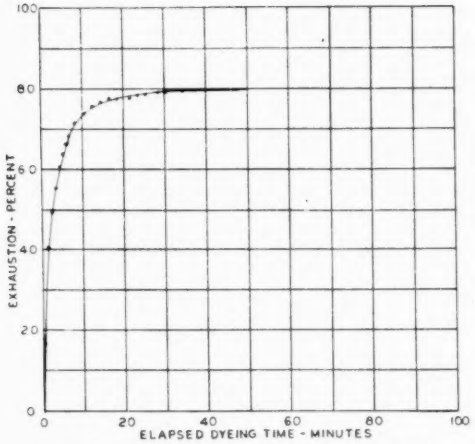

FIG. 16. *Curve for 0.5% Calcodur Red 8BL.*

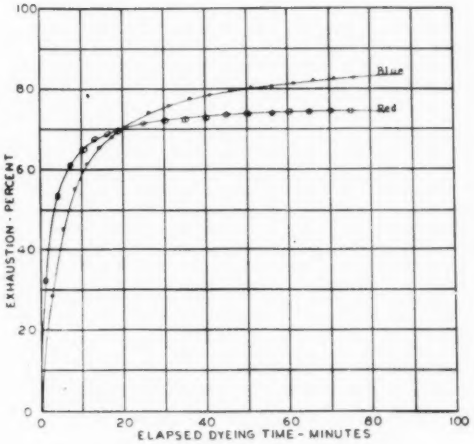

FIG. 18. *Curves for 0.5% Calcodur Red 8BL plus 0.5% Amanil Sky Blue FF.*

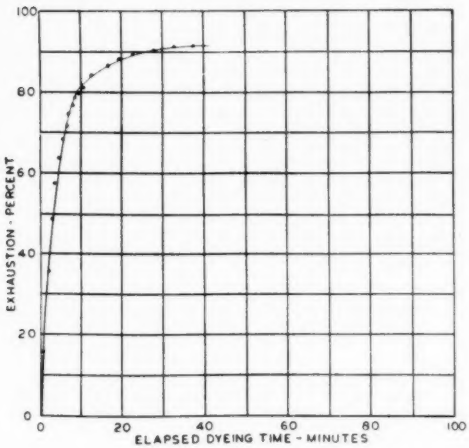

FIG. 17. *Curve for 0.5% Amanil Sky Blue FF.*

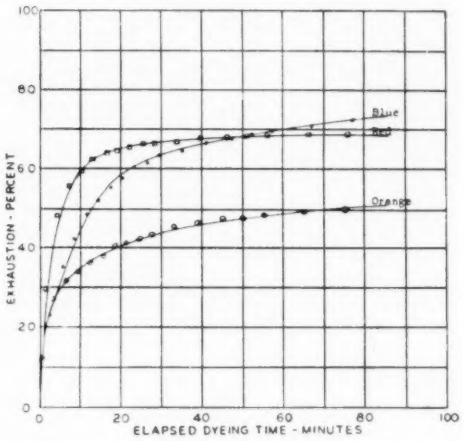

FIG. 19. *Curves for combination of 0.5% Calcodur Red 8BL, 0.5% Pontamine F. Orange ERL, and 0.5% Amanil Sky Blue FF.*

ferred to the cloth by means of engraved rolls. This is illustrated in Figure 12. With the aid of the specific gravity bottles, we are able to take an aliquot of the print paste, dilute it, and handle it in the same manner as that used for water-thin dye liquors.

Many other types of colored solutions are measured for control or investigative purposes. It is shown in Figures 10–12 that all solutions measured on the "spectro" contain 1% of a polyethylene oxide condensate (P.E.O.C.). This obviates the non-additivity in aqueous solution characteristic of mixtures of certain classes of organic dyes, thus permitting analysis of dye mixtures hitherto considered impossible. A discussion of the use of polyethylene oxide condensates was given in a previous paper [14]. Reflectance measurements on pile fabrics present a much more complex problem than those on almost any other textile by virtue of the enhanced third dimension—the pile. This means that the bulk of control work is done by the simpler transmission measure-

ments. In examination of unknown samples of cloth to determine qualitative information regarding the dyes used, the reflectance measurement is indispensable. Quantitative measurements of color change in numerous processes are made through the "spectro," but the complications involved do not lend themselves to good control methods.

Since the "spectro" does give an analytical representation of color, one might immediately assume that shade-matching is a natural realm of use for the instrument. This simple statement is true [11]; however, shade-matching involves many more mathematical complications than are commonly realized. The effects which an experienced dyer makes compensations for, based on his experience, must be separately considered in the analytical approach. To mention a few of the factors which are involved in using the "spectro" in matching dyed shades: we must know (1) the color of the original material and how it is affected in dying, (2) the color of the components, (3) the effect of dyeing conditions, and (4) the effect of measuring conditions. But despite all of the many things which must be considered, we were able to obtain excellent results in a practical way on flat worsted cloth.

We have found the "spectro" a convenient tool for studying the kinetics of dyeing. This has been fully discussed in a paper by Kienle, Royer, McCleary, and de Bruyne [6]. Our approach to the problem is more specific, since we are concerned mainly with the study of beck or box dyeing. We have developed a laboratory-model dyeing machine which gives fairly good correlation with production results. The amount of dye removed from a dye bath is determined spectrophotometrically by continuously examining the solution flowing through a special absorption cell. This is shown in Figures 13, 14, and 15. The cell is adaptable to most concentrations of dye liquors commonly used; the solution thickness can be varied from less than $^1/_{10}$ mm. to 11 mm. The whole apparatus is made from either 18% stainless steel or glass with pure gum rubber used where extreme flexibility is necessary. Data obtained from this dyeing machine must be translated and computed in order to arrive at results that have any meaning to the persons who are concerned with the application of dyes. A typical set of such curves is shown in Figures 16, 17, 18, and 19 (dyeing assistant, 10% common salt; temperature, 180°F).

In the application of spectrophotometry in the textile plant, emphasis is placed on the development of methods or procedures which have a maximum of utility. The spectrophotometer is the only instrument known at present which can measure color and we have only "scratched the surface" of its possibilities.

Acknowledgment

This is to acknowledge with appreciation the permission granted by Sidney Blumenthal & Company, Inc., to publish this material. This work would not have been possible without the able assistance of John Boyko and Marie Aquaro, as well as the excellent counsel of Harold H. Taylor.

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(*Manuscript received April 3, 1949.*)

A Study of Roving Coil Spacing on Bobbins

J. F. Bogdan*

Abstract

An equation, $C_c = 8.365H^{0.6617}$, makes possible the calculation of roving coils per inch for American carded cottons from a given roving number.

Relative roving density, width of coils, and rates of change are discussed. An application to a manufacturing problem is illustrated.

DETERMINATION of the proper roving lay, or number of coils of roving per unit length along one layer wound on a bobbin in the cotton manufacturing operation, has been accomplished generally by the application of individual judgment in manufacturing. Attempts have been made to standardize experience by the use of a set of constants, which when multiplied by the square root of the hank roving give a product which is said to indicate the proper number of coils per inch. These constants are stepped for progressive groups of roving sizes and serve as class multipliers; the effect which necessitates the change in multiplier has not been treated as a continuous variable.

E. B. Grover† completed a survey of actual manufacturing practice and obtained data for coils per inch for roving made from carded American cottons. These values were averaged, plotted against the corresponding roving sizes, and a smooth curve was drawn through the points for a range of roving sizes from 1.0-hank to 10.0-hank (Figure 3). The values shown in columns 1 and 2 of Table I were picked off this chart and comprise the data for this analysis.

Discussion

The factors to be considered in a study of roving coils per inch are: (1) shape of roving cross section, (2) roving size or weight, (3) degree of compactness or density of the roving, and (4) space between adjacent coils.

A strand of roving wound on a bobbin is not circular in cross section but is flattened by the winding tension, the presser foot, and the succeeding layers of windings. The actual shape of the roving cross section is not known, but it is assumed, for the purposes of this analysis, that it approximates an ellipse whose minor axis is perpendicular to the axis of the bobbin (Figure 1).

The equation for the area, A, of an ellipse is $A = \pi ab$. If the ratio of the major to the minor axis is assumed to remain constant regardless of roving size, then

$$A = k_1 a^2. \tag{1}$$

Shown below are the relationships which exist between weight (W), area of cross section (A), roving density (B), and roving size (H) expressed as the number of units of 840 yards (hanks) in 1 pound of material:

$$W \propto AB,$$

$$W \propto \frac{1}{H},$$

$$AB \propto \frac{1}{H},$$

and

$$\frac{1}{H} \propto k_1 a^2 B,$$

or

$$\frac{1}{H} = k_2 a^2 B.$$

The value for the major axis is

$$2a = D = 2\sqrt{\frac{1}{k_2 HB}},$$

where D is the width in inches of a flattened coil.

$$D = \frac{k_3}{\sqrt{HB}}. \tag{2}$$

The primary equation for coils per inch (C) is

$$C = \frac{1}{D + S}, \tag{3}$$

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where S is the space between adjacent coils in inches (Figure 2).

Substituting the value for D from equation (2) in equation (3),

$$C = \frac{\sqrt{HB}}{k_3 + S\sqrt{HB}}. \tag{4}$$

The ideal manufacturing arrangement of roving coils is considered generally to be such that adjacent coils just make contact when subjected to the winding pressures. The separating space S then has a value of zero, and equation (4) for this condition becomes

$$C = k_4\sqrt{HB}. \tag{5}$$

The square root of the density now can be expressed in terms of coils per inch and hank number:

$$\sqrt{B} = \frac{C}{k_4\sqrt{H}}. \tag{6}$$

Roving density is a function of the amount of twist inserted in the strand. As the material is drafted in the roving operations, the total effect of the cohesive force between fibers is lessened. To make up this loss in strength to an extent sufficient to allow the material to be drawn off the supply package without pulling apart, twist is added. Twisting the strand of roving causes an increase in the degree of compactness or density. The rate of change of density with respect to twist is high for low twists when the material is loose and fluffy and is low for high-twist roving where the density of the strand approaches a practical maximum for manufacturing.

The relationship $T = k\sqrt{H}$, where T is the number of turns of twist per inch, k is a constant multiplier, and H is the roving number in hanks per pound, is utilized in textile manufacturing. But twist is proportional to $\sqrt{H}$ for a constant multiplier only if the density remains constant. Since a change in twist causes a change in density, the above relationship is not valid and must be modified for effect of density change to obtain better approximations.

In normal cotton manufacturing only enough twist is inserted into the roving to allow the material to be drawn from the supply package to the drafting rolls without pulling apart; excessive twist causes drafting troubles. As the size of the roving becomes finer, twist must be added progressively. Therefore, twist and, in turn, density are functions of roving size. A general formula for the relationship between twist and roving size would be

$$T = kH^x,$$

where x is an exponent whose value might be determined from experimental data.

Since density is a function of roving size under normal manufacturing conditions,

$$B = k_5H^y; \tag{7}$$

$$\sqrt{B} = k_6H^{y/2}. \tag{8}$$

Substituting this value of $\sqrt{B}$ in equation (5),

$$C = k_7H^{1/2+y/2}. \tag{9}$$

If the exponent $n = \frac{1}{2} + \frac{y}{2}$,

$$C = k_7H^n. \tag{10}$$

Results

Coils per Inch

The values for the constants k_7 and n can be determined by substitution of values in the equation

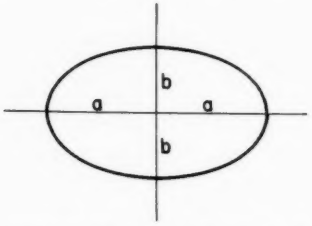

FIG. 1. *Idealized shape of cross section of flattened roving strand wound on a bobbin.*

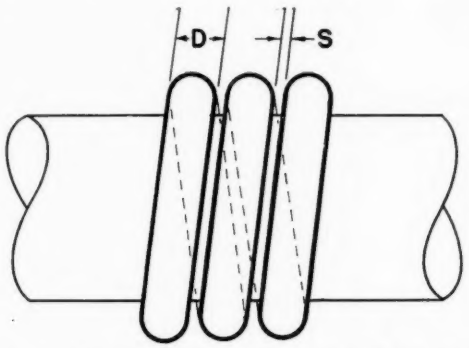

FIG. 2. *Schematic drawing of arrangement of first-layer coils on a roving bobbin.*

TABLE I. RELATIONSHIP BETWEEN PROPERTIES OF ROVING COILS AND ROVING NUMBER

(1) Hank roving H	(2) Coils per inch (observed) C	(3) Coils per inch (calculated) C_c	(4) Relative density kB	(5) Width of coils (in.) D	(6) Rate of change of coils with respect to hank $\frac{dC}{dH}$	(7) Rate of change of relative density with respect to hank $k\left(\frac{dB}{dH}\right)$	(8) Rate of change of width of coils with respect to hank $\frac{dD}{dH}$
0.2		2.9	0.282	0.345	9.54	29.71	1.1470
0.5		5.3	0.380	0.189	7.00	15.99	0.2503
1.0	8.5	8.4	0.475	0.119	5.54	10.00	0.0791
2.0	13.1	13.2	0.594	0.076	4.38	6.26	0.0250
3.0	17.2	17.3	0.678	0.058	3.82	4.76	0.0128
4.0	20.9	20.9	0.744	0.048	3.48	3.91	0.0079
5.0	24.3	24.3	0.799	0.041	3.21	3.37	0.0055
6.0	27.5	27.4	0.848	0.036	3.02	2.98	0.0040
7.0	30.4	30.3	0.891	0.033	2.87	2.68	0.0031
8.0	33.1	33.1	0.930	0.030	2.74	2.45	0.0025
9.0	35.7	35.8	0.967	0.028	2.63	2.26	0.0021
10.0	38.2	38.3	1.000	0.026	2.54	2.11	0.0017

$$\log C = \log k_7 + n \log H. \tag{11}$$

The values of the constants are found to be $k_7 = 8.365$, $n = 0.6617$.

The final equation for average coils per inch for roving made from American cotton becomes:

$$C_c = 8.365H^{0.6617}, \tag{12}$$

or

$$\log C_c = 0.9224 + 0.6617 \log H. \tag{13}$$

Substituting values for H in this formula gives the C_c values shown in column 3, Table I, which are in good agreement with the given values.

It will be noted that equation (12) is an example of the Power Law, so that plots of C_c vs. H on log-log paper would give a straight line.

Density

An expression for density of a strand of roving can be obtained in terms of hank number by determining the value of the exponent y in equation (7) from the value of n in equation (12).

$$n = 0.6617 = \frac{1}{2} + \frac{y}{2}, \quad y = 0.3234;$$

therefore

$$B = k_8 H^{0.3234}. \tag{14}$$

It is not possible to determine the value of the constant k_8 without additional information, but the expression can be modified to show relative density ($k_8 B$). A constant was selected which gave a relative density of unity for 10-hank roving. The

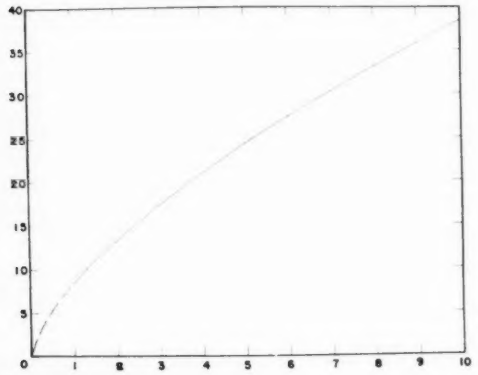

FIG. 3. *Relationship of roving coils per inch to roving size. Abscissa—hank roving (H). Ordinate—coils per inch* (C).

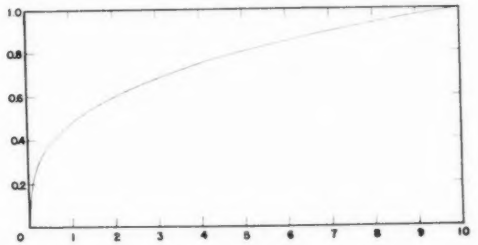

FIG. 4. *Relationship of relative density to roving size. Abscissa—hank roving (H). Ordinate—relative density* (KB).

formula so modified is

$$k_9B = 0.4749H^{0.3234}. \quad (15)$$

Calculated values for relative density are shown in column 4, Table I, and are plotted in Figure 4.

Width of Coils

The average width in inches of a coil of roving wound on a bobbin and compressed by succeeding layers is the reciprocal of the coils per inch when they just touch.

$$D = \frac{1}{C} = \frac{1}{8.365H^{0.6617}}$$

$$= 0.1195H^{-0.6617}. \quad (16)$$

Calculated values for roving coil widths in inches are shown in column 5, Table I.

Rates of Change

Having established the foregoing formulas, it is possible to obtain expressions for rate of change of one variable with respect to another by differentiation.

The rate of change of coils per inch with respect to roving size is obtained by differentiating equation (12).

$$\frac{dC}{dH} = 5.535H^{-0.3383}. \quad (17)$$

The rate of change of relative density with respect to roving size is obtained from equation (14).

$$k_{10}\left(\frac{dB}{dH}\right) = k_9H^{-0.6766}.$$

When k_9 is given an arbitrary value of 10, the equation becomes:

$$k_{10}\left(\frac{dB}{dH}\right) = 10H^{-0.6766}. \quad (18)$$

Rate of change of roving coil width with respect to hank roving number is obtained by differentiating equation (16).

$$\frac{dD}{dH} = -0.0791H^{-1.6617}. \quad (19)$$

The minus sign merely indicates that the width of the coils decreases with increase in roving number, and the sign was omitted from the calculated values shown in column 8, Table I.

Manufacturing Applications

The proper number of coils per inch for a given roving number for normal cotton manufacturing practice can be obtained by picking off a chart similar to Figure 3, or from a set of tabulated values calculated from equation (13).

A widely used manufacturing formula for the determination of the number of teeth in the lay gear required when the roving size is changed on a roving frame is

$$L_r = L_a\frac{\sqrt{H_a}}{\sqrt{H_r}}, \quad (20)$$

where L_r is the number of teeth in the gear required, L_a is the gear on the machine, H_a is the hank roving being made, and H_r is the hank roving specified to be made.

The above relationship again assumes that there is no change in density between H_a and H_r. So long as the change in roving size is small, the formula has practical value, but for many manufacturing changes, especially in the size of coarse rovings where the rate of change of density with respect to roving size is high, equation (20) requires correction.

Introducing the density factor gives:

$$L_r = L_a\frac{\sqrt{H_aB_a}}{\sqrt{H_rB_r}}, \quad (21)$$

or

$$L_r = \sqrt{(L_a)^2\cdot\frac{H_aB_a}{H_rB_r}}, \quad (22)$$

where B_a is the density of the roving being made, and B_r is the density of the roving specified. Relative densities may be used for B_a and B_r.

The effect of this change can be illustrated by an example:

Example

What lay gear is required on a roving frame when changing from 0.5-hank roving with a lay gear of 28 teeth to 1.0-hank?

Substituting in equation (22),

$$L_r = \sqrt{(28)^2\frac{(0.5)(0.380)}{(1.0)(0.475)}} = 17.7 \text{ or } 18 \text{ teeth.}$$

Equation (20) gives a result of 19.8 or 20 teeth, a difference of 11% in this instance.

Acknowledgment

The author is indebted to Prof. E. B. Grover for permission to reproduce Figure 3.

(*Manuscript received June 27, 1949.*)

An Inclined-Plane Yarn-Tester with Linearly Increasing Stress

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AFTER the International Congress on Rheology held at Scheveningen, September, 1948, about forty participants in the Congress visited the A.K.U. Research Laboratory at Arnhem, where some rheological measuring apparatus were demonstrated to them.

It appeared that they were very interested in our A.K.U. Inclined-Plane Tester, an apparatus operating *with constant rate of stress*.

Therefore, we think it advisable to give more general publicity to the principle underlying the operation of this apparatus. Particularly with respect to the theoretical treatment of stress-strain curves of threads by means of model theories, this apparatus, with the aid of which experimental data can be obtained, is very useful [1].

The A.K.U. Inclined-Plane Tester was developed about 1934 by our Textile Department in cooperation with our Instruments Workshop. Originally, it was intended as an apparatus in which the force on the thread increases in linear relation with the time.

Similar inclined-plane testers have been commercially available for a considerable time (*e.g.*, the well-known Scott Seriplane Tester). They work according to the principle that the thread under examination is fixed to a car with additional weight (total weight = G), which car rides on an inclined-plane with variable inclination. For an angle of inclination = α, the force P exerted on the thread is (when neglecting frictional and inertia forces):

$$P = G \sin \alpha.$$

If we want this force P to increase linearly in relation to the time, $\sin \alpha$ must increase linearly in relation to the time.

According to this principle the apparatus can be constructed in various ways. The structure of the Scott Tester, for instance, is quite different from that of the A.K.U. Inclined-Plane Tester. It is, however, not this point which interests us here. What we are interested in is the following: How can a normal inclined-plane tester operating *with steadily increasing force* be changed into an inclined-plane tester operating *with steadily increasing stress* (= force divided by the cross section of the thread under examination). Some years ago the auxiliary apparatus required for this purpose was added to our A.K.U. Tester. We are pleased to be able to give the description of this auxiliary apparatus, which, if desired, can be added to any other inclined-plane tester.

If, during the elongation process, not the force P exerted on the thread but the stress σ in the thread is to increase linearly in relation to the time, a special apparatus is required which continuously corrects the force P, depending upon the change in cross section of the thread under examination, which change in cross section occurs in consequence of the increase in length.

Let the "relative extension"—*i.e.*, the extension expressed as a fraction of the length in the original state—be equal to ϵ. When it is further assumed that the volume remains constant during the extension process of the thread, the area of the cross section of the thread at a relative extension ϵ will become $\frac{1}{1+\epsilon}$ times as large. If the stress in the thread is to be kept independent of the extension, the force on the thread must also become $\frac{1}{1+\epsilon}$ times as large; hence, the force P must be decreased by an amount $\frac{\epsilon}{1+\epsilon} P$.

It is schematically shown in Figure 1 how this has been accomplished. Parallel to the rail R_1, over which the car I with total weight G moves, a second rail R_2 has been provided, over which a

second car with total weight fG moves (in our apparatus $f = \frac{2}{5}$); the rail R_2 lies in the same inclined plane as the rail R_1 (perspectively shown in Figure 1).

Besides the thread under examination, a second cord, d_1, has been fixed to the car I; this cord has been wrapped around the disc S_1 (radius = R) and has been fixed to this disc at a. The disc S_1 has been fixedly mounted on the shaft b, on which a second disc, S_2, has been solidly fixed.

A cord d_2 has been fixed to the car II; this cord has been laid around the frictionless roller S_3 and has been fixed to the disc S_2 in the spot corresponding with the axis of rotation.

The shape of the disc S_2 is such that when extension of the thread under examination occurs the distance m—*i.e.*, the distance from the point where the cord d_2 comes into contact with the disc S_2 to the axis of rotation—increases (m is at right angles to the cord d_2).

Imagine the roller S_3 at an infinitely great distance. The auxiliary apparatus will then perform its task exactly when the following relation applies:

$$f \cdot P \cdot m = \frac{\epsilon}{1 + \epsilon} \cdot P \cdot R.$$

Thus, for a given clamping-in length of the test thread the shape of the disc S_2 can be calculated from the formula:

$$m = \frac{\epsilon}{1 + \epsilon} \frac{R}{f}. \tag{1}$$

If the original length of the thread under examination is equal to l_0, the angular displacement φ (in radials) of the shaft b, when a relative extension ϵ occurs, will be equal to:

$$\varphi = \frac{\epsilon l_0}{R}$$

or

$$\epsilon = \frac{R\varphi}{l_0}. \tag{2}$$

When substituting equation (2) in equation (1), we obtain:

$$m = \frac{\varphi}{l_0 + R\varphi} \cdot \frac{R^2}{f}. \tag{3}$$

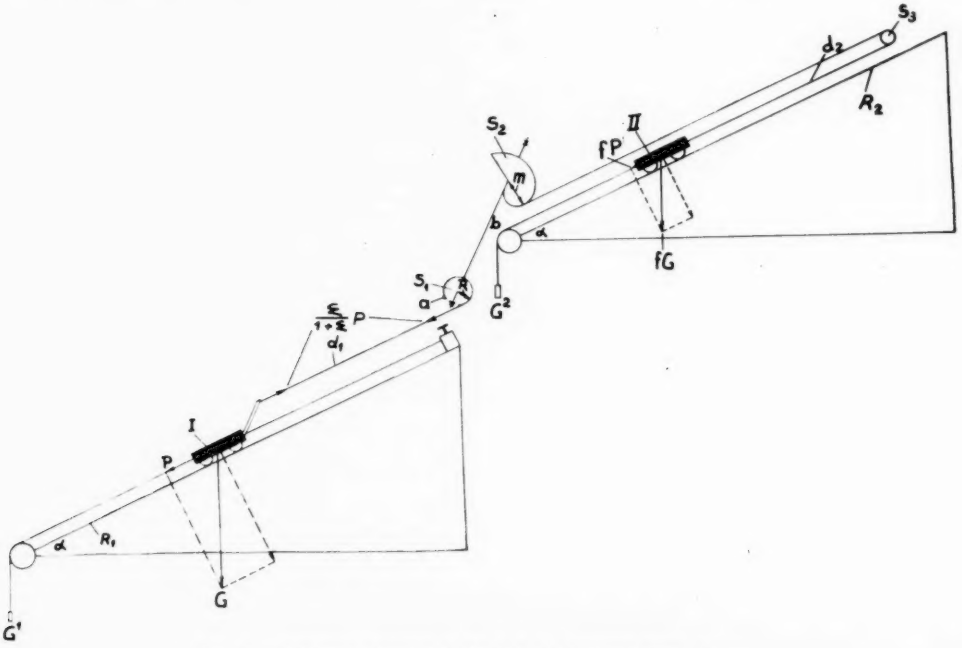

FIG. 1. *Schematic drawing of the A.K.U. Inclined-Plane Tester.*

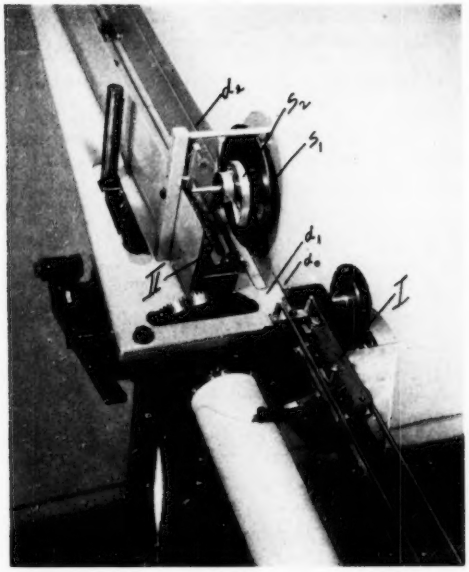

FIG. 2. *Photograph of the A.K.U. Inclined-Plane Tester.*

Thus, the shape of the disc S_2 should exactly fulfill formula (3); such a disc can be easily manufactured by means of a milling machine.

Actually, the roller S_3 is not infinitely far away, but—in our apparatus—at a distance of 50 cm. from S_2; hence an error results, which in our apparatus amounts to some tenths of a percent only, which amount can be neglected.

It may be remarked that the weights G^1 and G^2 in Figure 1, which are very small, serve only for keeping the cords d_1 and d_2, respectively, taut.

In Figure 2 the embodiment of the inclined-plane tester is represented. The clamping-in length of the thread under examination, d_0, amounts to 50 cm. For the meaning of the other letters refer to Figure 1.

Although in the case of a normal inclined-plane tester (constant rate of force) ϵ can be calculated as a function of the stress σ [2, 3], yet we always start in such cases from an experiment in which the stress σ does not increase linearly with the time t.

However, when stress-strain curves are treated mathematically, one usually starts from a linear relationship between σ and t, in order to obtain formulas which can be integrated in as simple a way as possible.

Thus, with the aid of the apparatus described above the experimental conditions are appreciably better adapted to those theoretically assumed (in this case $\sigma = ct$) than was usually possible until now.

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Manuscript received April 6, 1949.

Book Reviews

Absorption Spectrophotometry. G. F. Lothian. London, Hilger & Watts, Ltd. (Hilger Division), 1949. 196 pages; 76 illustrations. Price, $7.60.

(Reviewed by E. I. Stearns, American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey)

The new book *Absorption Spectrophotometry* by G. F. Lothian has much to recommend it. It contains explicit instructions regarding all laboratory procedures relating to transmittancy measurements. It tells how instruments work, what solvents to use, how to purify them, what types of solution cells are available, how to attain the best accuracy, and how to interpret and analyze data. These detailed instructions should prove very useful to one engaged in actual laboratory work. In addition, the book reviews briefly the history of absorption measurements and the theory underlying the correlation of chemical nature and absorption spectra of compounds. Hence one interested in the theoretical interpretation of spectra would also benefit from the book. It is particularly pleasant to find that the author treats the whole gamut of wave lengths, ultraviolet, visual, and infrared, as a single subject and draws examples from any range which happens to illustrate his point at the moment. Adequate references are given for further study.

One drawback from the viewpoint of a worker in this country is that, as would be expected of a Hilger publication, the instruments which are stressed are the Spekker Ultra-Violet Photometer and medium quartz spectograph for the ultraviolet, the Hilger Nutting Spectrophotometer for the visual, and the Hilger Industrial Infra-Red Spectrophotometer for the infrared. The instruments which are in much more extensive use in this country, such as the Beckman and Cary for the ultraviolet and visual, the Coleman and General Electric for the visual, and the Perkin-Elmer, Baird, and Beckman for the infrared, are dismissed with a paragraph or two apiece. The book would be more useful in this country if the emphasis were reversed. Another instance of a different viewpoint between Great Britain and the United States is in the discussion of solvents. The book contains instructions for eliminating impurities in methyl alcohol. In this country methanol is available in tank-car quantities at purities sufficient for absorption spectrophotometry. Two other weaknesses of the book for workers in this country are the lack of information on the measurement of reflecting samples and the omission of any discussion of colorimetric analysis of spectrophotometric curves —that is, an analysis leading to color specifications.

The book suffers somewhat from its brevity. Four examples of this shortcoming follow.

1. In the discussion of the necessary accuracy of a cell length for photoelectric measurements, the conclusion is drawn that an accuracy of 0.15% is adequate. This figure is based upon measurements of transmittancies. A more extensive treatment of the subject, including measurements relative to a standard solution of lesser concentration, would indicate the desirability of a greater length precision.

2. In discussing the optimum absorbency for precision to determine concentration, the author draws the conclusion that the optimum value is 0.4343. This value is derived for those instruments for which the response is linearly related to radiant flux. A more extensive presentation of the subject would include a discussion of those instruments using a Martens photometer and would lead to the conclusion that a greater density is optimum for these instruments.

3. In the section on methods of calculation the treatment could profitably be expanded. The author is to be commended for including discussions of analysis in the event of failure of Beer's Law and for the analysis in the presence of unidentified substances which can be assumed to have an absorption curve of constant first derivative over the analytical wave length. However, while the author warns of failure of additivity of two components by association or chemical interaction, he does not tell how to handle such cases. The treatment of multi-component analyses in this section deals with the case of a different wave length for each component but omits mention of analysis for multi-components at a single wave length by multi-solutions.

4. The discussion of purification of solvents omits

the use of silica gel. This is particularly useful for the preparation of cyclohexane of ultraviolet purity.

The nomenclature used in the book is somewhat different from that recommended in this country, and the figures are not consistently labeled within the book with respect to either abscissa or ordinate, but this is not unusual in the literature of absorption spectrophotometry.

In short, the book is probably valuable for laboratory workers in England and interesting to all absorption spectrophotometrists in the United States.

The Story of Silk. William F. Leggett. New York, Lifetime Editions, Inc., 1949. 361 pages. Price $5.00.

This is the fourth book in a series dealing with the development of textiles by William F. Leggett, Associate Technical Editor of *Rayon and Synthetic Textiles*. A foreword by Daniel E. Douty, President of the U. S. Testing Company, states that "Mr. Leggett has made a real contribution to our textile literature." As a matter of fact, this book is the only historical narration on the subject of silk. This is not a technical treatise, but it is an excellent historical treatment of silk, its origin, and sources by countries.

In the first chapters the author discusses the art of sericulture, the silk fiber, the silk moth and its cocoon, wild silk moths, and the mulberry tree. Then follows a discussion of the legendary and early history of the use of silk in the countries of the Far East, including its adoption by the Arabs and the Hebrews. The author then proceeds to trace the history of silk in Greece, Rome, Byzantium, Sicily, Italy, Spain, France, England, Germany and the Low Countries, and America. This is followed by brief notes on silk lace and a short glossary of silk names in general use. There is also a bibliography of books dealing with the subject of silk.

The book, as a whole, should be delightful reading to all those interested in the history of silk and its influence in all parts of the world. It is appropriate at this time when silk is about to stage a comeback.

Rayon Revue. English Edition. Published by International Rayon Trading Corporation, Arnhem, Velperweg 76, Holland. 64 pages.

The International Rayon Trading Corporation, sales organization for the AKU, commenced in March, 1947, to publish in the Dutch language *Rayon Revue*, a bi-monthly journal devoted to the production and processing of rayon and other man-made fibers and yarns. It is planned to publish once a year an English-language edition in which will appear a selection of the best articles of common interest.

This, the first issue in this series, carries a selection from the 1947 volume of *Rayon Revue*, and a description of the progress of the Netherlands rayon industry from 1930 to 1940. There are also a number of technical papers, with titles as follows: "Sampling of Natural and Synthetic Fibers"; "Determination of Denier and Strength of Single Filaments by Vibroscope and Heim Tensile Tester" (translated and first published in TEXTILE RESEARCH JOURNAL, July, 1947); "The Determination of Twist"; "The Significance of Skein Strength"; "Processing of Highly Twisted Yarns"; and "Running-Up of Twist in the Knitting of Rayon Yarns."

Copies of this issue, while they last, are available to the American industry without charge.

ABSTRACTS

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A list of periodicals, the abbreviations used in reference to articles, and the addresses of publishers of English-language publications is given in the January, 1949, issue, page 46.

ANALYSIS: TESTING: LABORATORY METHODS

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Abrasion Testing Machine

Improved single-unit Schiefer abrasion testing machine. Herbert F. Schiefer, Lawrence E. Crean, and John F. Krasny. TEXTILE RESEARCH JOURNAL **19**, 259–69 (May 1949).

An improved single-unit Schiefer abrasion testing machine has been developed which can be adapted for testing a great variety of materials under a wide range of test conditions. Different types of specimen holders and abradants can be used with the machine. Both the pressure and the tension on the specimen can be fixed at selected values and maintained constant throughout the test period. A variety of materials, including woven, knitted, and coated fabrics, plastics, paper, leather, and other materials, were abraded with the machine. The abrasive wear of each material was found to be extremely uniform over the abraded area. The effect of the amount of plasticizer on the resistance to abrasion of plastics was readily measured. The rate of abrasion was directly proportional to the amount of plasticizer present. The abrasive wear in tests of woven fabrics appeared very similar to that which occurred in service. A quantitative method based upon the change in electrical capacitance of the specimen with abrasion was described for evaluating the amount of abrasion. A quantity which is a measure of abrasive destruction or ruin was defined. This quantity was used to obtain an iso-ruin map of a large area of a trouser leg. This iso-ruin map showed very clearly a number of areas at which excessive wear in service had occurred. The change of the abradant during abrasion tests is discussed. Carborundum paper, a generally used abradant, decreased very greatly in abrasive power. The spring steel blade abradant remained essentially constant, although in testing one resin-finished fabric the surfaces of this abradant became coated with the resinous substance, which greatly increased its abrasive power. Authors

Text. Research J. Sept. 1949

Elastic Constants by Ultrasonic Methods

Determination of the elastic constants of solids by ultrasonic methods. W. C. Schneider and C. J. Burton. *J. Applied Phys.* **20**, 48–58 (Jan. 1949).

The application of ultrasonic methods to the determination of the elastic constants of solids is considered in some detail. It is shown that a rotating-plate technique in which ultrasonic transmission is plotted as a function of the angle of incidence of the waves allows determination of the velocities of the dilatation and shear waves in the plate. From these data, Poisson's ratio and the mechanical moduli are given. The elastic constants of several metals have been measured with this equipment and the values obtained are shown to be in agreement with previously published data. In addition, measurements of a number of thermoplastic and thermosetting resins have been made successfully. It has been found that in the case of Melmac Resin 26-8B there is no variation in the elastic constants as a function of cure time. Authors

Text. Research J. Sept. 1949

Measurement by Electronics

Advance textile production through electronics. Anon. *Am. Wool and Cotton Reptr.* **13**, 14–16 (Mar. 31, 1949).

Recently proven successful has been a recording instrument which will continuously record relative humidity from a point remotely located from the point of measurement. Electronic instruments may now be used to measure continuously such quantities as regain in yarn and cloth, pH in water or chemical solutions, concentration of chemical solutions, dry-bulb, wet-bulb, and dew-point temperatures, relative humidity, flow, and pressure. One of the best examples of the measure-

ment and control of such variables is exemplified in the automatic-controlled slasher room.

A. L. Landau

Text. Research J. Sept. 1949

Use of a Trellis Model in the Mechanics of Materials

The use of a trellis model in the mechanics of homogeneous materials. K. Weissenberg. *J. Text. Inst.* (Transactions) **40**, T89–110 (Feb. 1949).

A mechanical model, referred to as a trellis, is used to simplify the mathematical treatment of the classical theory of mechanics in accounting for the behavior of materials under mechanical actions. The trellis consists of two intersecting series of parallel rigid rods, pin pointed to one another where they cross, which are capable of extending and contracting in certain directions without a change in the length or the form of the rods. A comprehensive scheme is developed in which the classical theory and the theory of the trellis are united.

L. P. Witnauer

Text. Research J. Sept. 1949

A trellis model for the application and study of single pulls in textile materials. G. E. Chadwick, S. A. Shorter, and K. Weissenberg. *J. Text. Inst.* (Transactions) **40**, T111–60 (Feb. 1949).

The behavior of textile fabrics and other materials in the form of plane sheets when subjected to simple pulls is investigated. Each sheet is examined both at rest and free from mechanical actions and at some stressed and strained state. A trellis model is derived for the special two-dimensional case under consideration. Experimental techniques used in studying the stresses and strains are described.

L. P. Witnauer

Text. Research J. Sept. 1949

Second-Order Transition Temperatures of Polymers

Refractometric determination of second order transition temperatures in polymers. III. Acrylates and methacrylates. R. H. Wiley and G. M. Brauer. *J. Polymer Sci.* **3**, 647–51 (Oct. 1948).

A refractometric technique for determination of second-order transition temperatures (*Tm*) of polymers has been extended to include a series of alkyl acrylate and methacrylate polymers with transition temperatures down to −50°C. A convenient method of determining refractive index down to −75°C is described. Certain long-chained polymers are birefringent below *Tm*. Correlations of brittle point with *Tm* and relations between viscosity and *Tm* are reported.

Authors

Text. Research J. Sept. 1949

Refractometric determination of second-order transition temperatures. IV. Butadiene-acrylonitrile copolymers. R. H. Wiley and G. M. Brauer. *J. Polymer Sci.* **3**, 704–7 (Oct. 1948).

The second-order transition temperatures for 14 commercially available butadiene-acrylonitrile copolymers with 18–50% acrylonitrile have been determined refractometrically and found to be somewhat lower than the corresponding brittle temperatures. The data show a linear relation between second-order transition temperatures and acrylonitrile content.

Authors

Text. Research J. Sept. 1949

Determination of Sulfur in Viscose

Determination of sulfur in viscose. K. Krüger. *Kunstseide u. Zellwolle* **25**, 370–1 (1947) (through *Chem. Abstr.* **43**, 1566*e* (Feb. 25, 1949)).

Total S is determined volumetrically by titrating for total Na before and after oxidation to H_2SO_4 with H_2O_2, or gravimetrically by oxidation in the presence of NH_4OH, acidification with HCl, and precipitation with $BaCl_2$. Oxidation can also be carried out with alkaline hypobromite. A rapid plant method for xanthate S consists in casting a 2-g. film of cellulose xanthate, washing with 50 cc. of 40% $(NH_4)_2SO_4$ until clear, dissolving in 70 cc. of 0.5*N* NaOH, neutralizing with 1.5*N* HOAc, adding 10 cc. of 0.1*N* I_2 solution, 10 cc. of 1.5*N* HOAc, and 200 cc. of H_2O, and titrating with *N* $Na_2S_2O_3$. The temperature should be kept below 15°C and the analysis must be quickly terminated after neutralization with HOAc. A more precise method consists in reaction of *cellulose xanthate* with diethylchloroacetamide and determination of the N content of the reaction product.

Text. Research J. Sept. 1949

CHEMICAL and PHYSICAL RESEARCH

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Refractive Index of Cellulose

Refractive index of cellulose fiber. VI. The type of change in refractive indexes by the elongation of wet fiber in the air. S. Okajima and S. Yokoyama. *J. Soc. Chem Ind. Japan* **44**, 985–9 (1941); cf. *C.A.* **42**, 2428*e*. **VII. Influence of polymerization degree on the change of refractive indexes of the fiber stretched in wet state.** S. Okajima and H. Sakata. *Ibid.* 1039–43 (1941). **VIII. Effect of humidity.** S. Okajima and Y. Kobayashi. *Ibid.* **46**, 941–3 (1943). **IX. Change in refractive index of isotropic regenerated fiber stretched under water.** S. Okajima, J. Kumura, and S. Kobayashi. *Ibid.* **48**, 85–6 (1945). **X. Change in refractive indexes of isotropic dry fiber.** *Ibid.* 86. **XI. Change in refractive indexes of anisotropic fiber by wet stretching.** *Ibid.* 86–7. **XIII. Change in micelle orientation of wet yarn by wet stretching.** S. Okajima. *Ibid.* **49**, 167–8 (1946). **XIV. Relation between the anisotropy and the micelle orientations at the moment of breaking by drawing artificial fiber.** *Ibid.* 168 (through *Chem. Abstr.* **42**, 7037*h*–7039*a* (Sept. 20, 1948)).

(See *Chemical Abstracts* for complete abstract.)

Text. Research J. Sept. 1949

Electron Microscope Photographs of Natural Cellulose Fiber

Electron microscopical studies of natural cellulose fibers. W. G. Kinsinger and C. W. Hock. *Ind. Eng. Chem.* **40**, 1711–16 (Sept. 1948).

Beaten pulps from ramie, lint cotton, cotton linters, and chemical wood pulp have been examined by the electron microscope. Three methods of preparing the specimens were used—metallic shadow casting, surface replicas, and electron stains. 15 photographs are reproduced, at magnifications of 13,500–120,000 ×. Fine fibrils whose diameters varied from 90 to 400 Å are shown. Larger fibrils, such as are observed in the light microscope, are composed of bundles of these finer units. Periodic variations in structure at about 150 Å. along the long axis of the fibrils are revealed. The diameters of the fibrils in ramie, cotton, and wood pulp decrease in the order named. Variations in straightness and smoothness follow the same order. It seems significant that the accessibility to acid hydrolysis of ramie, cotton, and wood pulp correlates with the magnitudes of their fibrillar surfaces. Neither the width of the fibrils nor the lengthwise periodicity observed corresponds to the dimensions of the submicroscopic structures as determined by x-ray diffraction or physicochemical methods.

A. R. Macormac

Text. Research J. Sept. 1949

Ramie Cellulose

Loose positions (weak bonds) and their velocity of splitting in hydrolytically degraded ramie cellulose. E. Husemann. *Makromol. Chem.* **1**, 140–57 (1947); cf. C.A. **41**, 3961*b* (through *Chem. Abstr.* **42**, 7035*h* (Sept. 20, 1948)).

Purified ramie cellulose was hydrolyzed at 60°C with 0.5*M* $KHSO_4$ for various periods from 2 to 1,200 hrs. The η number (intrinsic η) of each product was calculated from the specific η in Schweizer reagent by means of the equation of Schulz and Blaschke (C.A. **36**, 17[9]). From the Staudinger equation the degree of polymerization (D.P.) of the products was found to decrease from 1,500 to 170. Mercerized ramie cellulose was hydrolyzed more rapidly. The D.P. of native ramie cellulose was estimated to be about 3,000. Because of the sensitivity of cellulose solutions to air, the hydrolysis products were converted into cellulose nitrates for further study. Fractional precipitations were made by the addition of water to solutions of cellulose nitrate in acetone, and the D.P. was determined for each fraction. The average value of K_m in the Staudinger equation was 8.1×10^{-4}, based on osmotic molecular weights of fractionated cellulose nitrates in acetone. A similar value starting with mercerized ramie cellulose was 9.7×10^{-4}. The distribution of chain lengths for several products is shown graphically along the curves calculated without the assumption of weak bonds. Slightly hydrolyzed and far-hydrolyzed products showed good agreement with the theoretical curves, but intermediate products were more uniform in D.P. Likewise, the nonhomogeneity function, U (cf. C.A. **37**, 5862[2]), showed that a considerable increase in uniformity of molecular weight occurred in hydrolysis products with a D.P. of 400–500. This finding is in agreement with earlier work (cf. C.A. **37**, 5861[6]) and indicates that at regular intervals of about 500 glucose units the cellulose molecule contains bonds which are faster-splitting than the normal glucosidic bond. The ratio of splitting velocities of normal to weak bonds was calculated to be about 1:5,000. The same ratio was obtained for mercerized ramie cellulose, although the rate of splitting was considerably higher.

Text. Research J. Sept. 1949

Properties of Cotton Fiber

Degree of polymerization, spiral structure, and strength of cotton fiber. Lyle E. Hessler, Marion E. Simpson, and Earl E. Berkley. TEXTILE RESEARCH JOURNAL **18**, 679–83 (Nov. 1948).

Cotton fiber from bolls collected on opening and dried in the laboratory without exposure to direct sunlight were tested for the following fiber properties: fiber length, fineness, strength, spiral structure, and degree of polymerization (D.P.). When these individual properties were each correlated with the Pressley strength index in simple correlations, the spiral structure and Pressley strength index gave the highest r values, and the degree of polymerization and Pressley index the second highest. For variety effects, the D.P. and Pressley index gave a higher coefficient of correlation than the spiral structure and Pressley index. Significant r values were obtained between fineness and Pressley index for total and variety effects, between fineness and D.P. for all effects, and between spiral structure and D.P. for all effects. Furthermore, a significant r value was found when fiber length was correlated with chain length (D.P.) for total over-all effects. It is concluded that the length of the cellulose molecule (D.P.), is an important factor in the physical properties of cotton fibers. All multiple correlations, including the fiber properties used in the simple correlations, were highly significant for varieties within locations and for over-all effects. Spiral structure and chain length (D.P.) when correlated with Pressley strength gave the highest coefficient of correlation.

Text. Research J. Sept. 1949 Authors

Dyes

A systematic investigation of the colour and dyeing properties of the aminoacridines. II. Diaminoacridines and substituted monoaminoacridines. C. L. Bird. *J. Soc. Dyers and Colorists* **64**, 357–9 (Nov. 1948).

The color and fastness properties on tanned cotton of a number of diaminoacridines and substituted monoaminoacridines, particularly derivatives of 5-aminoacridine, have been examined. Derivatives of 5-aminoacridine are almost always pale yellow and show better fastness to light and to wet treatments than do most basic dyes. Derivatives of *1-*, *2-*, *3-*, and *4*-aminoacridines and diaminoacridines exhibit a variety of hues—*e.g.*, rose and violet as well

as the familiar shades of yellow and orange—but they all show poor fastness to light and wet treatments. It should be borne in mind that the American method of numbering the acridine nucleus differs from the British method and that the 5-aminoacridine mentioned above would be 9-aminoacridine in America. Likewise the *1*-, *2*-, *3*-, and *4*-aminoacridines (American) would differ from the *1*-, *2*-, *3*-, and *4*-aminoacridines (British) mentioned above by the author. C. Amick

Text. Research J. Sept. 1949

Permanent Finishes

Permanent finishes on viscose rayon depending on cross-bonding. W. G. Cameron and T. H. Morton. *J. Soc. Dyers and Colourists* **64**, 329–36 (Oct. 1948).

The tensile rupture of a viscose rayon fiber occurs mainly by the irreversible slipping of adjacent cellulose molecules over each other. When such a fiber is impregnated with an acid-catalyzed urea-formaldehyde resin, the tendency for the molecules to slip over each other is altered. One school of thought (Meunier and Guyot) believes that this alteration may be due to cross-bonding. Another school (Wood) rejects the theory of cross-bonding and postulates that the change is due to the presence of amorphous resin deposited interstitially in the fiber. Cameron and Morton present evidence which they believe demonstrates the existence of cross bonds in the molecular structure of 9 modified viscose rayons. Cross-bonding is accomplished by treatments with (*a*) acid-formaldehyde, (*b*) borax, (*c*) acetone-formaldehyde, (*d*) urea-formaldehyde, (*e*) melamine-formaldehyde, (*f*) glyoxal, (*g*) ethyleneureas, (*h*) dimethylol-formamide, and (*i*) kaurit AF_1. One or more of these treatments is used for processing large quantities of rayon staple, yarn, or fabric to obtain (*a*) reduction of water retention, (*b*) dimensional stabilization, (*c*) "animalization" (imparting wool-like properties), and (*d*) crease-resistance. C. Amick

Text. Research J. Sept. 1949

Delayed Fracture

Delayed fracture of materials under tension, torsion, and compression. C. Gurney and Z. Borysowski. *Proc. Phys. Soc.* (*London*) **61**, 446–52 (Nov. 1948).

Delayed fracture of brass in ammonia vapor, polymethyl methacrylate in liquid carbon tetrachloride, and glass in air subjected to tension, torsion, and compression are investigated and the times to fracture under a series of constant loads are determined. The gradual spread of cracks is thought to cause the delayed fracture. Tension fractures in the test specimens were transverse and torsion fractures were helical. Fracture times for brass and glass subjected to tension and torsion are approximately equal at equal principal tensile stresses. For equal times to fracture the fracture of polymethyl methacrylate occurs at higher principal tensile stresses in torsion than in tension. Delayed fracture did not occur in compression. L. P. Witnauer

Text. Research J. Sept. 1949

Properties of Laminates

Tensile and compressive properties of laminated plastics at high and low temperatures. J. J. Lamb, I. Albrecht, and B. M. Axilrod. *Natl. Advisory Comm. Aeronaut., Repts., Tech. Mem. Notes*, Tech. Note No. 1550, 57 pp. (1948); cf. *C.A.* **41**, 1875*c*; **42**, 5255*g* (through *Chem. Abstr.* **42**, 8021*h* (Oct. 20, 1948)).

The materials tested were an unsaturated polyester laminate reinforced with glass fabric (*I*), phenolic laminates reinforced with asbestos fabric (*II*), high-strength paper (*III*), rayon fabric (*IV*), and cotton fabric (*V*). *V* was studied in both the high- and low-pressure types. The tensile strengths at 77°F ranged from 5,000 to 43,000 lb. per sq. in.; the strengths of *I*, *III*, and *IV* were about 3 times those of *II* and *V*. The compressive strengths of *II*, *III*, *IV*, and *V* at 77°F were 21,000 lb. per sq. in. ± 10%. The strength of *I* was 36,000 (crosswise) and 42,000 (lengthwise) lb. per sq. in. The tensile strengths of all the materials at −70°F were 15–33% higher than at 77°F, and the compressive strengths were 30–85% higher (the strengths of *I* and *II* were 30% higher). At 200°F, *I*, *III*, *IV*, and *V* showed tensile and compressive strengths which were approximately one-half of the corresponding values at −70°F; *II* showed much smaller changes. The tensile and compressive moduli of elasticity of *I* and *III* were greater than those of the other materials at all temperatures, and were in the range of 2.6×10^6 to 3.3×10^6 lb. per sq. in. The tensile and compressive moduli of all the materials increased more at −70°F than they decreased at 200°F, as compared to the 77°F values.

Text. Research J. Sept. 1949

Adhesion Between Polymers

The adhesion between layers of different polymers. K. Thinius. *Kunststoffe* **37**, 36–8 (1947) (through *Chem. Abstr.* **42**, 6570*e* (Oct. 10, 1948)).

Adhesion between layers of different high polymers can be effected (1) by offsetting the different polarities of the 2 layers by inserting between them a substance which combines in its molecule both polarities, or (2) by an intermediate layer which has in its molecule besides a polar group a nonpolar part of a higher radical weight than that of the polar group. The first method is usually realized by means of copolymers of monomers having different polarities: *e.g.*, a copolymer of vinyl chloride with an ester or an ether. Materials suitable for the second method are polymers of $CH_2{:}CRCO_2R'$ or $CH_2{:}CROCOR'$, where R is H or alkyl and R′ is a nonpolar radical larger than the rest of the molecule.

Text. Research J. Sept. 1949

Multichain Polymers

Synthesis of multichain polymers and investigation of their viscosities. J. R. Schaefgen and P. J. Flory. *J. Am. Chem. Soc.* **70**, 2709–18 (Aug. 1948).

A convenient general procedure for synthesizing non-linear condensation polymers of controlled structure is presented and the theoretical basis is discussed. The principle em-

ployed involves the co-reaction of an *A-B*-type monomer—*i.e.*, an amino acid or hydroxy acid with a small proportion of a multifunctional reactant of the type RA_b or RB_b, where R is a b-valent radical and A and B are co-reacting functional groups. Such a multifunctional reactant may be, for example, a polyamine or a polybasic acid. Polymers so produced can be represented by the formula

$$R[-A(B-A)_{\bar{y}}-]_b$$

or

$$R[-B(A-B)_{\bar{y}}-]_b.$$

These multichain polymer molecules are therefore composed of b chains of average length ($\bar{y}$ units), each radiating from the central radical (R). It is to be noted that network formation is precluded so long as the terminal group A or B, as the case may be, cannot co-react. The degree of branching is fixed according to the functionality of the central unit. The average length ($\bar{y}$) of the chain is controlled by the proportion of the multifunctional unit employed; it is also dependent upon the extent of condensation which, however, ordinarily is carried very nearly to completion. The multichain polymers employed were prepared from ε-caprolactam (instead of from the corresponding amino acid), using either a tetrabasic or octabasic carboxylic acid as the multifunctional reactant. For comparison, monochain and dichain ε-caproamide polymers (stearic and sebacic acids, respectively, were used as the multifunctional reactants) have been prepared as well. The various polymers for which data are reported herein can be represented by the formula

$$R[-CO(-NH(CH_2)_5CO-)_{\bar{y}}OH]_b,$$

where b is 1, 2, 4, or 8, $\bar{y}$ being varied in each case by manipulating the proportion of the multifunctional reactant. Cyclohexanone-tetrapropionic acid and the analogous octabasic acid were used in preparing the tetrachain and octachain polymers. Viscosity, weight fraction of the linear molecules, number-average and weight-average molecular-weight data for monochain, dichain, tetrachain, and octachain polymers are reported. The logarithm of the melt viscosity for a given series of polymers varies linearly with the square root of the weight-average molecular weight. The effect of branching on the melt viscosity and on the intrinsic viscosity relationship becomes noticeable only when the amount of branching is large—*i.e.*, when the branching functionality is increased to 8. Authors

Text. Research J. Sept. 1949

Water Absorption of Proteins

Water absorption of proteins. III. Contribution of the peptide group. E. F. Mellon, A. H. Korn, and S. R. Hoover. *J. Am. Chem. Soc.* **70**, 3040–4 (Sept. 1948).

The absorption of the peptide chain backbone is probably of the same magnitude, if not identical, for all long-chain polypeptides and proteins. Peptide groups appear to be responsible for about 45% of the vapor-phase water absorption by casein and for 70% of the absorption by zein at 60% relative humidity. An absorption isotherm is presented which permits linear interpolation between 30% and 80% relative humidity for all proteins and extrapolation to 100% relative humidity in a few special cases. Data on the vapor-phase water absorption of glycine peptide of 2–6 units in length show that non-hydroscopic amino acids may give hydroscopic peptides. A. R. Macormac

Text. Research J. Sept. 1949

Sericin

The isolation of sericin and some of the physical-chemical properties of sericin sols. W. Rauch. *Melliand Textilber.* **28**, 307–11 (1947) (through *Chem. Abstr.* **43**, 853*d* (Jan. 25, 1949)).

Sericin is almost completely removed from raw silk after 8 hrs. in boiling water. The resulting dilute sol can be concentrated to 10% solids by evaporation over an open flame. This solution gels on cooling. Dry powdered sericin can be prepared by injecting the solution as a fine spray into a blast of warm air. Two driers of this type are described. The extinction spectrum of sericin sol was determined. A sharp peak at 273 mμ was found, corresponding to tyrosine. The extinction constant *vs.* pH curve showed a maximum at pH 4.1. Viscosity, swelling, electrical resistance, and migration in an electric field were measured as a function of pH. The swelling and viscosity curves showed a minimum at pH 4.1. This is taken to be the isoelectric point. It is suggested that sericin be used as an adhesive and sizing material and as a culture medium in place of agar.

Text. Research J. Sept. 1949

BLEACHING: DYEING: FINISHING

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Textile Processing

Chemistry in textile processing. W. E. Prentice. *Can. Text. J.* **66**, 44–5 (May 13, 1949).

A brief account showing how chemistry is applicable to all textile processes, including wool scouring, piece and stock dyeing, carding, spinning, and finishing. L. A. Fiori

Text. Research J. Sept. 1949

Improving Slasher Production

Improving slasher production. Anon. *Am. Wool and Cotton Reptr.* **14**, 11, 12, 67 (Apr. 7, 1949).

The maximum production of a slasher is achieved through machine efficiency and the addition of supplementary equipment, such as extra carrying rolls, an extra cylinder, or a double headway. Slasher production in many cases may be increased by careful and close attention to details, such as steam pressure, condensate removal, and the characteristics of the sizing compound. Production over and above this maximum may be achieved by adding extra carrying rolls or another cylinder in order to increase the total area in which the yarn is in contact with the cylinder drying surface. Mills slashing

warps of slight construction may be able to double production through the installation of a double headway. A. L. Landau

Text. Research J. Sept. 1949

Color and Constitution

Color and constitution. Part XI. The aminocoumarins. H. H. Hodgson. *J. Soc. Dyers and Colourists* **65**, 14–17 (Jan. 1949).

The fact that all the aminocoumarins are yellow, whereas coumarin itself is colorless, may be readily explained by modern resonance theory, which provides also a qualitative explanation of differences in depth of color based on facility of resonance. The real cause of the color of aminocoumarin is probably to be found in the resonance between the auxochromic amino group and the chromophoric —O—CO— group, the carbonyl constituents of which greatly facilitate polarization and thereby promote the intergroup resonance. In consequence, the Kekulé resonance structures which prevail in the colorless coumarins are accompanied in the aminocoumarins by ionic quinoid structures which, on the Lewis-Calvin theory, are responsible for the visual color. The remarkable stabilities of the amino- and diaminocoumarins are a consequence of the resonance promoted by the combined action of amino and carbonyl groups. The rhythmic field effect which was suggested by Clayton to be the cause of the yellow color of the aminocoumarins is now shown to be without theoretical support.

Text. Research J. Sept. 1949 C. Amick

Dyeing Viscose

Some factors affecting the dyeing of viscose rayon. III. The volume swelling. J. M. Preston, S. H. Mhatre, and K. I. Narasimhan. *J. Soc. Dyers and Colourists* **65**, 17–20 (Jan. 1949).

It was observed by Preston and Kapadia (*J. Soc. Dyers and Colourists* **63**, 435 (1947)) that equilibrium dye absorption varied with the degree of orientation of viscose fibers. They concluded that the pores present in viscose fibers were elongated during spinning, and that the elongation of the pores was directly proportional to the orientation. As the pores were elongated, the closer the walls of the pores approached each other and the less the surface available to large dye molecules, with a consequent lowering in the equilibrium dye absorption. It was pointed out by Morton (*J. Soc. Dyers and Colourists* **63**, 438 (1947)) that if this mechanism were correct, then the more highly oriented fibers, which take up less dye, should swell less. The present authors have completed swelling and dyeing measurements and indices of refraction measurements on viscose rayon fibers which were spun with a range of volume swelling values from 60 to 150%. Dyeing isotherms were determined at 80°C using pure Sky Blue FF. Volume swelling values were obtained from the combined axial and transverse swelling data, and refractive indices of the fibers were measured by means of a fiber refractometer. These data offer a general confirmation of the experimental data presented in the previous paper. Furthermore, these data show that the highly oriented fibers do take up less dye and swell less. These dye absorption-volume swelling data have also been examined by means of the theoretical treatment of Marshall and Peters (*J. Soc. Dyers and Colourists* **63**, 446 (1947)). These data fit the theoretical curves well for the fibers with small to moderate swelling values but diverge markedly for the fibers with large volume swelling values. This indicates that for the fibers with high volume swelling values the total internal volume is greater than the effective volume associated with the cellulose surface which is being dyed. C. Amick

Text. Research J. Sept. 1949

Finishing Fabrics

Some defects arising in the finishing of woolen and worsted fabrics. C. S. Whewell. *J. Soc. Dyers and Colourists* **65**, 9–14 (Jan. 1949).

Recent developments in the science and technology of finishing have placed increasing responsibilities upon the finisher, for he must now understand the principles of an increasing number of widely differing techniques if he is to keep defective pieces at a minimum. Even so, close cooperation between spinner, manufacturer, and finisher is the best way to keep the number of defective pieces at a minimum. Some of the common faults discussed are those which may occur: (1) in the preliminary processes, such as damage by mice, rats, and mildew; (2) in the setting or crabbing processes, such as tension, temperature, and pH of the setting bath if uneven treatment and creases of undyed pieces or staining and bleeding of dyed pieces are to be avoided; (3) in the scouring process, where extreme care is needed to prevent oil stains, unevenly dyed pieces, lime soap stains, loss of handle, yellowing, color bleed, mildew, molding, chafing and staining, and particularly crease marks due to delayed drying; (4) in milling, defects such as chafing, tearing or "mill rigging," which show up as warp marks and are caused by localized felting increases; (5) in drying, where the most obvious defects which might occur are due to the material coming off the tenter pins, resulting in uneven tentering, possible staining, and need for reworking; (6) in the raising operation, to produce a pile or nap; and (7) in the finishing operation. C. Amick

Text. Research J. Sept. 1949

Heat-Setting Nylon Fabric

Heat-setting nylon fabric. Anon. *Am. Wool and Cotton Reptr.* **15**, 11, 12 (Apr. 14, 1949).

Nylon can be heat-set by several different methods and in different shapes and conditions to meet a wide variety of needs and uses. Heat-setting a nylon fabric causes a rearrangement and stabilized fixation of the internal molecular structure, which is the reason the fabric will retain its shape after continued use and laundering. Nylon yarn has a tendency to contract (approximately 9% to 10%) when heat-set. A. L. Landau

Text. Research J. Sept. 1949

Wool Scouring

Soap substitutes in the worsted industry. R. W. Moncrieff. *Soap, Perfumery & Cosmetics* **21**, 1114–15 (1948) (through *Chem. Abstr.* **43**, 2451g (Mar. 25, 1949)).

Petroleum derivatives, usually sulfates or sulfonates of fat alcohols and of ethylene oxide condensate-type of detergents for washing wool, are discussed.

Text. Research J. Sept. 1949

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

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Rayon Staple

New horizons for rayon staple. E. D. Dobbins. *Can. Text. J.* **66**, 42–5 (Apr. 1, 1949).

A general report on the applicability of staple rayon in blends with wool and cotton for the manufacture of new fabrics having increased market appeal. Adaptability of these blends to the cotton, woolen, worsted, flax, and jute systems is described briefly. L. A. Fiori

Text. Research J. Sept. 1949

Textile Keystones

Textile keystones. A. M. Tenney. *Papers of AATT* **4**, 22–30 (Dec. 1948).

An outline of the essential fiber properties of each of the filament fibers—rayon, estron, nylon, and silk—and the staple fibers—cotton, wool, rayon, estron, nylon, and silk—with respect to commercial value and consumer preference. Specific mention is made of the luster characteristics of these fibers. L. A. Fiori

Text. Research J. Sept. 1949

Filament Denier Factor in Nylon Fabrics

Filament denier factor in nylon fabrics. *Textile Manufacturer* **75**, 76–8 (Feb. 1949).

The characteristics and properties of a fiber are determined by its chemical composition and physical form. The cross-sectional shape of the fiber employed will be reflected in the texture of the fabric. The characteristics of nylon fiber with relation to physical structure are analyzed. A. L. Landau

Text. Research J. Sept. 1949

Use of Nylon on Woolen and Worsted Systems

Use of nylon on woolen and worsted systems. Anon. *Am. Wool and Cotton Reptr.* **10**, 11, 12, 48, 49 (Mar. 10, 1949).

Strength of lightweight fabrics may be increased by twisting woolen fiber around a core of nylon or by spinning blends of nylon and wool. The added strength obtained from the use of nylon may be utilized by making finer yarn of original strength or by increasing the strength of the fabric. Tables are shown comparing strength of yarns of different blends. A. L. Landau

Text. Research J. Sept. 1949

Weaving Tape Fabrics

Zip fastener tapes. A. Thompson and S. Bick. *Silk J. & Rayon World* **25**, 62–3, 65 (Feb. 1949).

Weave plans, construction details, and suggestions for making cam looms adaptable for the weaving of this type of tape fabric are described in detail. Designs are illustrated. *Text. Research J. Sept. 1949* L. A. Fiori

Vicara—A New Fabric

Vicara—a new fabric. G. R. Wildermuth. *Textile Bull.* **75**, 67–9 (Apr. 1949).

Vicara is a new textile fabric produced by the Virginia-Carolina Chemical Corporation. Vicara is a protein fabric produced by dissolving the protein in an alkaline solution and then extruding it through spinnerets into an acid-precipitating bath for coagulation. Due to its protein base, it more closely approaches the characteristics of wool than those of any other natural fiber. It may be used to make 100% yarn but is recommended for blending. The physical properties, chemical properties, and reaction to bleaching and dyeing are discussed. A. L. Landau

Text. Research J. Sept. 1949

Shuttle Projection

An experimental study of shuttle projection. I. H. Thomas and J. J. Vincent. *J. Text. Inst.* **40**, T1–29 (Jan. 1949).

A method is described for measuring the displacement of the shuttle and the rotation of the loom crank-shaft relative to time and to each other; from these measurements shuttle and loom speeds and accelerations can be derived. It was found that the initial and average shuttle speeds were approximately equal, ranging from 31 to 48 ft. per sec. on the 15 looms measured. The different speeds produced by different nose-bits were found to be approximately proportional to the nominal displacements after a 30° rotation of the crank-shaft. The shuttle speed was approximately directly proportional to the average loom speed during picking, approximately inversely proportional to the distance of the picking tappet from the packing shaft, and independent of the mass of the shuttle and the position of the buffer. The timing of the pick produced no effect if the sley were stationary, but under normal conditions unsystematic changes occurred, although on the whole a later pick gave a higher shuttle speed. Shortening the picking band and lowering the picking bowl usually increased the shuttle speed. With old picking bands prolonged weaving produced little change, but with new bands the shuttle speed became lower as weaving progressed, partially recovering during rest periods. Measurements of the acceleration of the shuttle showed, in a typical instance, a maximum deviation of 3.0 in. of the shuttle from its nominal position. The deviation increased with heavier shuttles and at higher loom speeds. The results were found to agree broadly with theory but there were appreciable detailed discrepancies. Possible causes of these are suggested, and a semi-empirical formula for shuttle speed of reasonable accuracy is derived. *Text. Research J. Sept. 1949* Authors

Checking Shuttles in Power Looms

The checking of shuttles in power looms. I. H. Thomas and J. J. Vincent. *J. Text. Inst.* **40**, T30–44 (Jan. 1949).

The checking of shuttles has been studied by obtaining the displacement time relation for the shuttle when it is being checked in the shuttle box. From this relation was obtained the maximum value of the retardation and the speed of impact of the shuttle with the picker. The position at which the shuttle came to rest was also observed. The maximum value of the retardation was found to vary from about 50g for a 45-in. loom fitted with a controlled swell adjusted to stop the shuttle just short of the picker to at least 220g for a 60-in. fast-reed loom with a plain swell (g is the acceleration due to gravity). The speed of impact of the shuttle with the picker was negligible with a controlled swell, but was high (up to 40 ft. per sec.) when plain swells were employed. The variation of the rest position of the shuttle over 1,000 picks was about $\frac{1}{2}$ in. to $\frac{3}{4}$ in. The use of an accelerometer giving direct readings of the maximum retardation is described, and comparisons of results obtained by the two methods are made. It is shown that the accelerometer may fail to respond to high transient values of the retardation, but this does not impair its usefulness for comparative purposes. Authors

Text. Research J. Sept. 1949

Merits of Dry and Wet Twisting

Merits of dry and wet twisting. Anon. *Textile Inds.* **113**, 127, 129 (Apr. 1949).

Wet twisting produces a smoother and more compact yarn than dry twisting. There are two methods of wet twisting: English, in which the yarn is wet and then taken to the twister rolls; and Scotch, in which the bottom roll is partially submerged to wet the yarn after it is on the roll. The hardness of water used in wet twisting will affect the amount of moisture taken up by the yarn. A. L. Landau

Text. Research J. Sept. 1949

Winding and Beam Warping

Winding and beam warping. E. Brierley. *Textile Weekly* **43**, 602, 604, 606, 608 (Mar. 18, 1949); **43**, 677–8, 680, 682 (Mar. 25, 1949).

Three items are discussed in full: (1) automatic cone winding, (2) automatic pirn winding, and (3) high-speed beam warping. Machine principles and aims, suggestions for efficient operating procedure, and other helpful ideas are discussed in detail. L. A. Fiori

Text. Research J. Sept. 1949

MISCELLANEOUS

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Blending

Accurate mixing with fiber meters. Anon. *Textile Bull.* **75**, 7, 8 (Apr. 1949).

A description of the blending unit designed and developed at the Marion Manufacturing Company. It is claimed that the fiber meters provide the pickers with an accurately balanced blend at all times. A. L. Landau

Text. Research J. Sept. 1949

Quality

A quality blend makes successful sales. J. R. Price. *Am. Dyestuff Reptr.* **38**, P234–5, P238–9 (Mar. 7, 1949).

With the passing of consumer hysteria due to war scarcity of many items, a buyer's market requires a proper blending of cooperation, product research and control, and factual information. Product research and control in the plastics industry has been necessary to prevent the marketing of materials or products which were inferior and which might damage finishes—*e.g.*, furniture—with which they came in contact. In 1941 the production rate of plastic film was 40,000 sq. yds. per mo., whereas today it is $15\frac{1}{4}$ million sq. yds. per month. 80% of the film produced was clear, whereas today at least 40% is colored. This increased use of plastics, both clear and colored, has resulted from careful research, control, and consumer information.

Text. Research J. Sept. 1949 C. A. A.

Textile Driers Studied by I. T. T.

Textile dryers studied by I. T. T. P. M. Thomas. *Textile World* **99**, 116–17 (Mar. 1949).

Charts compiled by the Institute of Textile Technology in a survey of textile driers are given. Steam-cylinder, hot-air, infrared, and high-frequency dielectric machines are compared, with reference to operational cost and efficiency. Steam was found to be the cheapest source of drying-heat and steam-heated cylinders the most practical form of drier. Better removal of moist air, more complete temperature control, and more efficient heat-transfer can improve present drying by as much as 20% it is claimed. A. L. Landau

Text. Research J. Sept. 1949

Tire-Cord Fibers

Man-made fibers in tire casings. J. W. Illingworth. *Trans. Inst. Rubber Ind.* **24**, 59–69 (1948) (through *Chem. Abstr.* **43**, 1209*e* (Feb. 10, 1949)).

A review and discussion of present developments in the replacement of cotton by synthetic fibers, particularly viscose rayon and nylon. The properties of important fibers are described, and tabulated data show the relative properties of various natural and synthetic fibers with respect to density, tensile strength, tenacity, hygroscopicity, heat resistance, adhesion to rubber, and price. Attention is called to the unfortunate tendency for the molecular orientation in synthetic fibers to be greater at the surface than in the interior, and it is suggested that if the central portion of the fiber were oriented to give the necessary strength of fiber and the outer layers disoriented to give flexibility, a fiber giving superior performance would be expected.

Text. Research J. Sept. 1949

Felt Flow Chart

Felt flow chart. Anon. *Textile World* **99**, 103–6 (Mar. 1949).

A flow chart is reproduced following the manufacture of wool felt. Felt ranges in density and properties from soft fabric to hard sheets, depending upon ultimate use. Processing methods are similar to yarn manufacturing in early stages and more closely resemble cloth finishing in final steps of manufacture.

A. L. Landau

Text. Research J. Sept. 1949

Progress in Knitting Machinery

Progress in knitting machinery. C. E. Johnson. *Textile Age* **13**, 28, 32, 34, 39, 42 (Apr. 1949).

During the last 3 yrs. new knitting machinery has been produced on a commercial scale, and most of the old-model machinery has been improved so that it can operate more economically at higher production and will produce better-quality fabrics. Full-fashioned hosiery machinery incorporates such new designs as automatic welt-turning, automatic hookup, automatic friction control, and higher speeds. Circular knitting machinery is built with double cylinders and a double-hilt needle so that it is possible to knit from either the top or bottom cylinder, making possible the production of an unlimited number of patterns. The machine is also designed with double feeds so that for every revolution of the cylinder two courses will be knitted. The knitting machinery produced by various concerns is discussed, and their design and the particular fabrics for which they are suited are described. A. L. Landau

Text. Research J. Sept. 1949

Sea-Water Laundering

New developments in Army sea-water laundering. T. H. Vaughn, E. F. Hill, C. E. Smith, L. R. McCoy, and J. E. Simpson. *Ind. Eng. Chem.* **41**, 112–19 (Jan. 1949).

Because of the military need of increasing the range and carrying capacity of our ships during World War II, emergency measures were taken by the Navy and the Army Surgeon General to do laundering aboard ships with sea water. Towards the end of 1944 the problem became so urgent that the Army Quartermaster General undertook an intensive research program to provide the best available products and to devise processes for this task. This paper describes the work done by and for the Quartermaster to this end. The lack of accepted laboratory methods for measuring detergency was considered a greater handicap than the critical shortage of detergent products. An extensive program was undertaken to advance the test methods, to evaluate all detergents that could be made available in quantities necessary for military requirements, and to devise optimum washing procedures for utilizing the most promising ones. The work was done in three phases: (1) laboratory detergency tests, (2) full-scale laundry operations with synthetic sea water, and (3) confirmation of pertinent findings under actual use conditions with sea water. As a result, 4 products were approved as suitable for military needs of sea-water laundering, and improved laundry formulas were developed for all the major classifications of military clothing.

Text. Research J. Sept. 1949 Authors

Plasticity

Recent developments in the mathematical theory of plasticity. W. Prager. *J. Applied Phys.* **20**, 235–41 (Mar. 1949).

30 references.

Text. Research J. Sept. 1949

Spinning Calculations

Spinning calculations simplified. Part 7. Anon. *Platts Bull.* **6**, 134–9 (Mar. 1949).

Previous charts numbered 1–44 of this series are included in Parts 1–6. (See *T.R.J.* **19**, 380 (June 1949).) This report contains charts 45–8. These graphs indicate: (1) turns per inch for a normal range of hank rovings and twist multipliers employed on slubbing, intermediate, and roving frames, and (2) twist gear required for a range of turns per inch used on these roving frames.

Text. Research J. Sept. 1949 L. A. Fiori

Tapered Paper Tubes

Tapered paper tubes here to stay. Anon. *Am. Wool and Cotton Reptr.* **7**, 15–16 (Feb. 17, 1949).

It is claimed that there is a very definite and rapid trend toward the use of tapered paper tubes and sleeve-type spindles for spinning frames, particularly warp. The need for the top suspension drive as obtained by tapered paper tubes was not discovered until the advent of high-speed, long-draft, and large-package spinning. Advantages resulting from the use of paper tubes are said to be: (1) decreased bolster wear, (2) lowered spindle wear, (3) saving of power, (4) less vibration, and (5) longer traveler life.

A. L. Landau

Text. Research J. Sept. 1949

Automatic Looms

High practical speeds claimed for Belgian automatic loom. Anon. *Silk J. & Rayon World* **25**, 42–3 (Feb. 1949).

A brief account of a new automatic loom having simplified mechanical features and adaptable to the weaving of rayon and other synthetics, cotton, linen, and mixtures. Alternatively, the loom is also adaptable for dobby and jacquard weaving. Its outstanding feature is optimum picking speeds, ranging from 110 with a 108-in. reed to 220 with a 36-in. reed. L. A. Fiori

Text. Research J. Sept. 1949

Molded Plastic Quills

Moulded plastic quills. Anon. *Textile Manufacturer* **75**, 59 (Feb. 1949).

Molded plastic bobbins and quills are claimed to be accurately and uniformly formed, smooth-surfaced, stable under changes of atmospheric conditions, nonflammable, available in various colors for identification purposes, and without metal ferrules. The discarded bobbins may

be ground up and remolded to another pattern. A. L. Landau
Text. Research J. Sept. 1949

Photographic Aids

Photographic aids to the textile industry. M. Siegel. *Am. Dyestuff Reptr.* **38**, P268–73 (Mar. 21, 1949).

The author discusses the value of photography in: (1) making records, such as photostating, microfilming, fiber-length distribution in staples, microscopical examination, and training aids; (2) in high-speed motion picture and high-speed still picture photography, such as pick motions, check straps, cam action, flight of shuttle, and many other processes which may occur at such a rapid rate that it is impossible to study them with the human eye; (3) the special uses of intermittent, infrared, ultraviolet, and fluorescent photography, as well as electron micrographs and x-ray diffraction. Various systems for high-speed work are discussed in some detail. The work of Millson and Royer, which includes a method using fluorescent dyes for diffusion studies, is described in some detail. C. A. A.
Text. Research J. Sept. 1949

Tendering by Light

The action of light on textile materials—a review of the literature. D. K. Appleby. *Am. Dyestuff Reptr.* **38**, 149–56, 189–92 (Feb. 21, 1949).

Sunlight is generally conceded to be the most active factor in causing deterioration of exposed textiles. Since photochemical action produces changes on textiles primarily of a chemical nature, it would seem that this effect could be reduced or even eliminated by treatments capable of inhibiting or preventing the photochemical action. The findings of 232 papers, recorded since 1920, are reviewed under the headings: (1) radiation, (2) the role of oxygen, (3) other exposure conditions, (4) evidence of actinism on cotton, (5) bast fibers, (6) wool, (7) silk, (8) cellulose acetate, (9) cellulose nitrate, (10) viscose, (11) casein, vegetable protein, (12) glass, (13) acrylonitrile fibers, (14) polyamides, (15) polyesters, and (16) polyvinyls. Comparative ratings compiled from tables occurring throughout the literature and based on % loss in breaking strength showed that, generally speaking, wool showed less loss than any of the other fibers, whereas silk showed the most loss of the other fibers tested. 4 investigators placed cotton above rayon, 6 investigators placed cotton below rayon, and 2 investigators placed cotton and rayon on the same level. 2 investigators placed linen above rayon but 4 investigators placed linen below rayon. 3 investigators placed cotton below linen while 2 investigators placed cotton above linen and 1 investigator placed cotton and linen on the same level. As might be expected, much of the data are in disagreement, probably due to the fact that dissimilar experimental conditions were used.
Text. Research J. Sept. 1949 C. A. A.

Wool and Chlorine

Reaction between wool and active chlorine. D. Frishman, L. Hornstein, A. L. Smith, and M. Harris. *Ind. Eng. Chem.* **40**, 2280–4 (Dec. 1948).

Wool can be made resistant to shrinkage during laundering by treatment with solutions of active chlorine. The pH of such solutions is of importance in determining the type and extent of modification of the wool. The oxidation potentials of these solutions decrease with increasing pH, and the extent of modification of the fiber is found to be an inverse function of pH. The rate of reaction is also dependent upon pH and in addition the rates indicate that different types of reaction occur in the regions of pH 1, 3 to 7, and 9 to 11. The weight loss during treatment; alkali solubility; cystine, sulfur, and nitrogen contents; and acid- and base-binding capacities of the treated and untreated fibers confirm the difference between the reactions in these pH ranges. These data indicate that the treatment of wool with solutions of active chlorine can be most advantageously performed in the region of pH 8 to 9. Authors
Text. Research J. Sept. 1949

Cotton Research Program

Cotton plans a research program. L. Smith. *Am. Dyestuff Reptr.* **37**, P866–70, 878 (Dec. 27, 1948).

Two years ago in August, the Congress of the United States enacted into law the Agricultural Research and Marketing Act of 1946. To implement the act, Congress allowed an appropriation of $9,000,000 for the fiscal year 1948, and one of $13,850,000 for the fiscal year 1949. From this $22,850,000 the cotton textile mill owners, textile finishers, and suppliers of textile chemicals should expect to have available a continually increasing store of research knowledge. This paper deals with the story behind this program for cotton. In the production and marketing of cotton, the problems given highest priorities are: (1) mechanization of cotton production, (2) improved ginning of cotton, (3) improved cleaning of cotton prior to shipment to the textile mill, and (4) improved control of insect damage, which annually takes about $\frac{1}{7}$ of the total cotton crop. The Southern Regional Research Laboratory has research work under two rather general headings: (1) fundamental characteristics of cotton fibers, and (2) new and improved products. Under these two headings 11 research projects have been developed. In addition, the Secretary of Agriculture is authorized to contract with appropriate institutions for the conduct of research projects. 6 contracts have been placed with various agencies covering, among others, (*a*) improvement in resistance of cotton textiles to soiling, (*b*) application of infrared techniques to the study of deterioration of cotton cellulose, and (*c*) development of an improved instrument to determine the tensile strength of cotton fibers. In addition, 4 projects are planned for early consideration and possible letting of additional contracts: (1) improvement in the crease-resistance of cotton fabrics, (2) improvement in

the draping qualities of cotton fabrics, (3) improvement in luster of cotton, and (4) development of a satisfactory method for determining frictional properties of cotton fibers. C. A. A.

Text. Research J. Sept. 1949

Recent research on cotton properties at the Southern Regional Research Laboratory. K. Ward, Jr. *Am. Dyestuff Reptr.* **38**, P122–6 (Feb. 7, 1949).

This paper recounts certain phases of the research being carried on at the Southern Regional Laboratory under the Research and Marketing Act of 1946 (see preceding abstract). The first work, on tire-cord, has necessitated investigation on tensile strength, flex life, elongation, elasticity, and adhesive qualities, etc. The tensile strength of cotton has been increased by treatment with liquid ammonia or amines or by a special type of mercerizing treatment combined with stretching. Frequently, treatments that improve the tensile strength improve the other properties also. Mercerization, under proper conditions, appears to be the best treatment for improving flex fatigue at elevated temperatures, as well as tensile strength. Some work has been done to determine the so-called crystalline-amorphous ratio. These experiments indicate that most cottons contain about 85–90% crystalline cellulose. Work has been done on crease-resistance but details are not given. Weathering of gray cloth appears to be due to microorganisms, whereas weathering of finished fabrics or purified cotton fabrics appears to be due to the photochemical action of sunlight. Treatment of the fabrics with urea-formaldehyde resin is particularly effective in protection against weathering. Acetylating cotton fabrics to 21–22% inhibits microbial degradation. The program has included chemical treatments aimed at improving water-repellency and also methods of producing improved self-sealing fabrics. This latter project covers the evaluation and measurement of swelling. Thick-walled and thin-walled fibers swell approximately 25–30% in water. Occasionally thin-walled, "immature" fibers swelled only 20% whereas the thick-walled, "mature" fibers swelled 30%. These were separated by differential dyeing, where the thick-walled fibers dyed red and the thin-walled fibers dyed green. Cotton of high swelling ability can be produced by chemical modifications, such as by the addition of alkali and chloracetic acid. Properly etherified, the cotton swells without dissolving. Work of the Regional Laboratory on fireproofing is also discussed. C. A. A.

Text. Research J. Sept. 1949

Research Committee

157th general research committee meeting. *Am. Dyestuff Reptr.* **38**, P211 (Mar. 7, 1949).

The present status of work of A.A.T.C.C. research committees is given: (1) wash fastness, (2) light fastness, (3) perspiration fastness, (4) chemical analysis and testing, (5) fire-resistant materials, (6) flammability, (7) water resistance, (8) standard soil, (9) snag resistance, (10) non-woven fabrics, (11) visual aids, (12) insect pests, (13) dimensional restorability, and (14) color. C. A. A.

Text. Research J. Sept. 1949

Labeling Fabrics

Trade practice rules and procedures for textiles. H. Miller. *Am. Dyestuff Reptr.* **38**, P274–5, P280 (Mar. 21, 1949).

This report is by the Director of the Bureau of Trade Practice Conferences and Wool Act Administration of the Federal Trade Commission, who states that there exists as a matter of law the overriding principle that all labeling (of textiles) is required to be truthful and free from deceptive or misleading tendencies or effects. This applies irrespective of whether the label is of the voluntary or obligatory class. The subject is discussed under the following topics: (1) the coordinated principles of rules, (2) the wool products labeling act, (3) the rayon rules, (4) and the silk and linen rules. These 4 sets of rules cover not only the individual fibers but any combination which may contain one of them. The methods of testing and test procedures are discussed in some detail. C. A. A.

Text. Research J. Sept. 1949

Sizing Women's Garments

A system for the sizing of women's garments. M. L. Staples and D. B. DeLury. TEXTILE RESEARCH JOURNAL **19**, 346–54 (June 1949).

Body measurements for a representative number of American women (over 10,000) have been analyzed and a system is proposed for the sizing of women's garments based on this analysis. Size classes for the entire population of women 18 years of age and over have been developed in terms of independent control dimensions which are essential for the proper fit of the particular type of garment considered. Dimensions have been computed for standard forms set up to represent each size class of the population. The calculations involve the use of the control variables and certain dependent variables required to define the size and and shape of each mannequin. A scheme for identifying the different size classes is also proposed. This scheme takes advantage of the fact that body measurements may be divided into three categories which are virtually independent of one another. Authors

Text. Research J. Sept. 1949

Changes in Yarn Numbers

New changes in denier and filament numbers of American synthetic yarns. H. R. Mauersberger. *Rayon and Synthetic Texts.* **30**, 44–6 (Mar. 1949).

Presented are tables listing all American producers of viscose, acetate, and cuprammonium yarns, and the deniers and filament numbers of the yarns as they are actually produced and sold. Also tabulated are the semi- and high-tenacity yarn producers and the deniers and filament numbers they offer. Some significant trends are disclosed.

Text. Research J. Sept. 1949 L. A. Fiori

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